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XXXIV. *The Hall Effect, Electrical Conductivity, and Thermoelectric Power of the Copper-Tin Series of Alloys.*

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Introduction.

THE Hall effect, electrical conductivity, and thermoelectric power of the copper-tin series of alloys have been determined with the object of comparing the curves showing the relation between these properties and composition of the alloy with the curves already obtained for the copper-antimony alloys[†]. The curves showing the relation between the electrical property and the composition of the alloy generally furnish singular points corresponding to compounds formed of the two metals. Two compounds, Cu_2Sb and Cu_3Sb, are formed of the two metals Cu and Sb, while Cu_3Sn and Cu_4Sn are considered to be the compounds formed of the metals Cu and Sn. The crystal structure of Cu_3Sn and Cu_4Sn has been examined by Westgren and Phragmén[‡]. Cu_4Sn was found to have a face-centred cubic structure, with 416 atoms in the unit cell, while Cu_3Sn has an hexagonal close-packed structure. Jones and Evans* examined the structure of Cu_3Sn and Cu_3Sb, and their results for the Cu_3Sn were in very close agreement with the other workers. They found that the structure of both Cu_3Sn and Cu_3Sb was hexagonal close-packed, with the same axial ratio.

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[*] Communicated by Prof. E. J. Evans, D.Sc., University College of Swansea.

[†] Stephens and Evans, Phil. Mag. vol. vii. Jan. 1929.

[‡] *Zeits. für Metallkunde*, Sept. 1926.

The electrical properties of metals and alloys depend on their physical state. In the present experiments the electrical resistivity was determined for the alloys after preparation, and was afterwards redetermined for each alloy after annealing at a suitable temperature. This was repeated until further annealing produced no change in the resistivity. The temperature coefficient of resistance, Hall effect, and thermoelectric power were then determined for the alloys in the final state.

The curve showing the variation of the electrical conductivity with the composition of the copper-tin series of alloys has been obtained by Lodge †, Matthiessen ‡, and Ledoux §, and singular points were obtained corresponding to Cu_3Sn and Cu_4Sn.

Experimental Work.

The copper used for making the alloys was of electrolytic origin, while the Chempur tin contained ·0115 per cent. impurities. The impurities were copper ·0005 per cent., lead ·003 per cent., bismuth ·0005 per cent., antimony ·0055 per cent., and iron ·0020 per cent. The alloys were chill cast in an iron mould in the form of plates, about 15 cm. long, 3·0 cm. wide, and ·4 cm. thick. The alloys near the compounds were very brittle, and plates were difficult to prepare, so that in most cases the mould was heated before pouring the alloy. All the alloys were approximately uniform, and the mean values of their dimensions, determined at regular intervals along them, were taken. The plates of alloys near the ends of the series could be machined, so that thin plates in a convenient form for determining the Hall coefficient could be obtained.

In these experiments plates were cast of the following percentage composition by weight :—(1) 90 per cent. Cu, 10 per cent. Sn ; (2) 80 per cent. Cu, 20 per cent. Sn ;

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* Phil. Mag. vol. iv. Dec. 1927.

† Phil. Mag. vol. viii. p. 554 (1879).

‡ Landolt Bornstein, vol. ii. p. 1058.

§ *Comptes Rendus*, vol. clv. (1912).

(3) 72·8 per cent. Cu, 27·2 per cent. Sn (Cu_5Sn); (4) 68·1 per cent. Cu, 31·9 per cent. Sn (Cu_4Sn); (5) 65 per cent. Cu, 35 per cent. Sn; (6) 61·6 per cent. Cu, 38·4 per cent. Sn (Cu_3Sn); (7) 57·2 per cent. Cu, 42·8 per cent. Sn (Cu_5Sn_2); (8) 34·8 per cent. Cu, 65·2 per cent. Sn (CuSn); (9) 100 per cent. Sn.

The same plate of an alloy of given composition was used in the determination of all the electrical properties.

(1) *Electrical Resistivities and Temperature Coefficients of Resistance of the Alloys.*

The electrical resistivity was determined by fixing a plate of the alloy across two knife-edges, and determining the resistance of a known length by means of the Kelvin Bridge. All determinations were made at 0° C., and the values of the resistivities in the initial and final states of the alloy are given in Table I. and Graph I.

TABLE I.

Composition of alloy.	Resistivity before annealing, in microhms per cm.^{3} at 0° C.	Resistivity after annealing, in microhms per cm.^{3} at 0° C.	Annealing temperature in ° C.
100 % Sn....................	11·1	—	—
(*a*) SnCu (34·8 % Cu) ...	11·3	10·95	155
(*a*) Sn_2Cu_5 (57·2 % Cu) ...	9·12	8·93	180
(*a*) $SnCu_3$ (61·6 % Cu) ...	10·5	8·72	565
(*b*) $SnCu_3$ (61·6 % Cu) ...	11·3	8·67	565
(*a*) 35 % Sn, 65 % Cu ...	19·2	26·0	565
(*a*) $SnCu_4$ (68·1 % Cu) ...	48·5	47·8	565
(*a*) $SnCu_5$ (72·8 % Cu) ...	37·5	35·8	500
(*a*) 20 % Sn, 80 % Cu ...	24·8	25·2	500
(*c*) 10 % Sn, 90 % Cu ...	13·1	15·0	750
100 % Cu ...	1·59	—	—

(*a*) Annealed in coal-gas.
(*b*) ,, ,, vacuum.
(*c*) ,, ,, nitrogen.

The mean temperature coefficient of resistance over the range of temperature between 0° C. and 100° C. was determined for each alloy in its final state, and these results are given in Table II. and Graph II. The resistivity determinations have been made with an accuracy of about $\frac{1}{3}$ per cent. The larger temperature coefficients of resistance have been determined within approximately $\frac{1}{3}$ per cent., while the low values for the alloys in the region between Cu_4Sn and 90 per cent. Cu, 10 per cent. Sn are accurate to within 2 per cent.

Graph I.

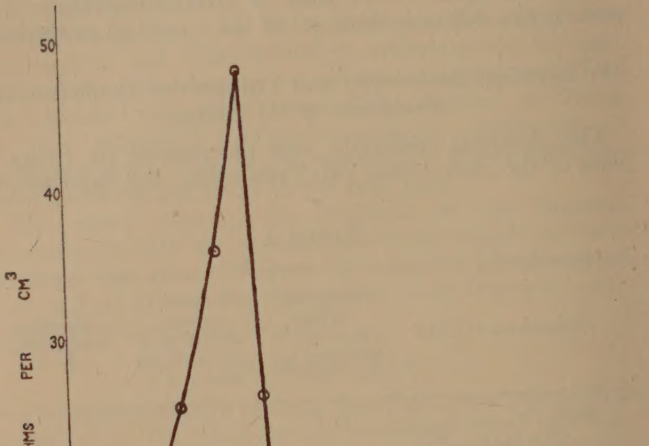
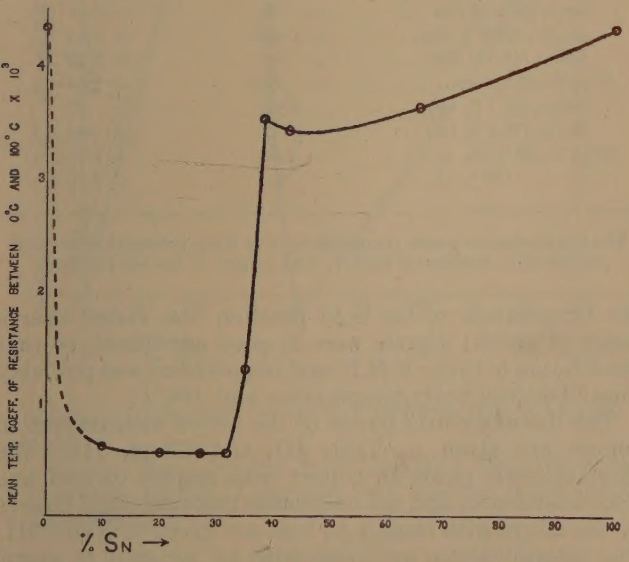


TABLE II.

Composition of alloy.	Mean temperature coefficient of resistance between 0° C. and 100° C. × 10^4.
100 % Sn	43·3
SnCu (34·8 % Cu)...	36·3
Sn_2Cu_5 (57·2 % Cu).	34·3
$SnCu_3$ (61·6 % Cu) .	35·3
35 % Sn, 65 % Cu	13·0
$SnCu_4$ (68·1 % Cu) .	5·72
$SnCu_5$ (72·8 % Cu) .	5·88
20 % Sn, 80 % Cu	5·74
10 % Sn, 90 % Cu	6·25
100 % Cu	43·5

GRAPH II.



(2). *Thermoelectric Power of the Alloys.*

The thermoelectric properties of the alloys were examined with copper leads soldered to the ends of the plates. The copper-alloy junctions were enclosed in two jackets, by means of which one junction could be kept at the temperature of steam and the other at the temperature of running tap-water. Repeated determinations of the thermo-E.M.F. of the copper-alloy couples over this range of temperature were made by means of a Tinsley vernier potentiometer. The determinations of the thermoelectric power in micro-volts per degree centigrade when the temperature of the cold junction was varied over a range of several degrees were in good agreement, so that the relation between E.M.F. and temperature was probably linear between room-temperature and 100° C.

Table III.

Composition of alloy.	Thermoelectric power with respect to Cu, in microvolts per degree centigrade.	Thermoelectric power with respect to Pb, in microvolts per degree centigrade.
100 % Sn	— 3·28	— ·12
SnCu (34·8 % Cu) ...	— ·75	+ 2·41
Sn_2Cu_5 (57·2 % Cu)...	— ·269	+ 2·89
$SnCu_3$ (61·6 % Cu) ...	+ ·06	+ 3·22
35 % Sn 65 % Cu	— ·612	+ 2·55
$SnCu_4$ (68·1 % Cu) ...	— 2·99	+ ·17
$SnCu_5$ (72·8 % Cu) ...	— 2·72	+ ·44
20 % Sn 80 % Cu	— 2·06	+ 1·10
100 % Cu ...	0	+ 3·16

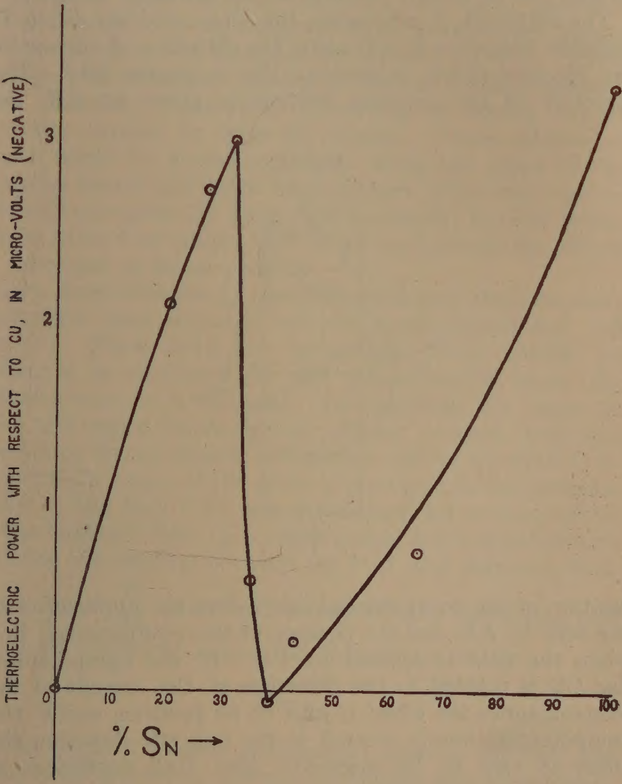
The thermoelectric power is considered +ve if the potential of the cold copper-alloy junction is positive with respect to the hot junction.

The thermoelectric power of the alloys with respect to copper are given in Table III. and Graph III. The thermoelectric power of copper with respect to lead was also determined, and the calculated thermoelectric powers of the alloys with respect to lead are given in Table III. The determinations are made with an accuracy of about 1 per cent.

(3) *Hall Effect of the Alloys.*

When a metal plate conveying an electric current is placed in a magnetic field, so that the lines of force are normal to the conducting plate and to the direction of flow of the electric current, a transverse galvanomagnetic potential difference is set up between the edges of the plate.

Graph III.



It has been proved experimentally that for a given metal the Hall P.D. denoted by E is given in abs. units by the formula

$$E = \frac{RHI}{d},$$

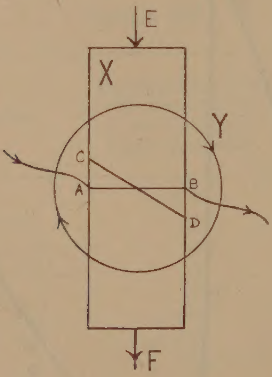
where H is the magnetic field in gauss, I is the current in abs. units, d is the thickness of the plate in cm., and R is the Hall coefficient.

This coefficient R depends on the temperature, and, for some metals, on the intensity of the magnetic field as well.

It is of importance to note that the effect has different signs in various metals, and the convention with regard to sign can be readily understood by reference to fig. 1.

The rectangle X represents the plate, and the circle Y, with the arrowheads indicating the direction of current in the electromagnet, represents the magnetic field. The direction of the primary current is given by EF, the position of the equipotential line before the application of the field by AB, and the position of this equipotential line when the field is applied by CD. If the equipotential line CD is rotated in the direction of the current in the electromagnet the effect is said to be positive, and if the equipotential line is rotated in the opposite direction the effect is said to be negative. The Hall coefficient is negative for both copper and tin, the value for tin being about 4 per cent. that for copper.

Fig. 1.



The Hall effect for the copper-tin alloys is very small. Since the Hall P.D. is inversely proportional to the thickness of the plates, and very thin plates could not be prepared, a very sensitive galvanometer was required, and consequently a delicate Paschen galvanometer was used in the present experiments. It was mounted on a stone pillar, at a distance of 7½ metres from a large circular electromagnet which had been rotated into such a position that its effect on the galvanometer was a minimum. This electromagnet, excited by a current of 6 amperes, produced a field of 8500 gauss in the 1·5 cm. air-gap between the pole-pieces of circular section having a diameter of 9 cm.

The alloy plate under investigation was rigidly fixed in a vertical position in the magnetic field by two brass clamps which also served as leads for the primary current. These clamps were fixed to a wooden frame which also supported the secondary electrodes, consisting of spring copper contacts carried by bars of ebonite. These electrodes, which could be moved vertically along the edges of the plate by means of a screw arrangement, were connected to the galvanometer by long, well-insulated, flexible wires. These wires were pulled taut so as to eliminate the effects of vibration as far as possible.

In a determination of the Hall coefficient the secondary electrodes were adjusted on the equipotential line AB (fig. 1). Then, with the secondary circuit closed, no deflexion is produced in the galvanometer when the primary current is reversed. On applying the magnetic field and again reversing the primary current, with the secondary circuit closed, a deflexion due to the Hall P.D. between the edges of the plate is produced in the galvanometer. The Hall P.D. was determined for several values of the magnetic field up to 8000 gauss, and a graph drawn showing the relation between the P.D. and magnetic field. The value of $\frac{\mathrm{E}}{\mathrm{H}}$ could be determined from this graph, and the Hall coefficient calculated from the equation

$$\mathrm{R}=\frac{\mathrm{E}d}{\mathrm{HI}}.$$

The primary current (4 amperes) passing through the plate could be read on a Weston ammeter with an accuracy of about 1 in 1200. The magnetic fields corresponding to various currents passing through the electromagnet were determined by a search-coil and Grassot fluxmeter. The absolute value of the magnetic field when a current of 2 amperes passed through the magnet was determined by means of a delicate ballistic galvanometer and a search-coil of known mean area, and from this result corrections could be applied to the fields as determined by the flux-meter. The magnetic field determinations are considered to be correct within about one-half per cent.

The Hall effect was determined at room-temperature, the exact temperature being observed by an accurate thermometer suspended with its bulb in contact with the plate.

The experimental results for the Hall coefficients are given in Table IV. and Graph IV.

TABLE IV.

Composition of alloy.	Thickness of plate in cm.	Hall coefficient.	Temperature of plate in ° C.
100 % Sn	—	—·000020*	—
SnCu (34·8 % Cu)...	·2370	+·000264	13·1
Sn_2Cu_5 (57·2 % Cu).	·4150	+·000775	18·9
$SnCu_3$ (61·6 % Cu)..	·4136	+·000935	13·1
35 % Sn, 65 % Cu	·4145	+·000713	15·6
$SnCu_4$ (68·1 % Cu)..	·4095	+·000802	17·7
$SnCu_5$ (72·8 % Cu)..	·4100	+·000139	14·4
20 % Sn 80, % Cu	·2562	—·000262	17·9
100 % Cu	—	—·000520*	—

* Campbell, 'Galvomagnetic and Thermomagnetic Effects.'

It is, however, important to point out that in addition to the Hall potential difference a transverse galvano-magnetic temperature difference is set up between the edges of the plate. This is the Ettingshausen effect, and is usually very small. The difference of temperature, ΔT, is given by

$$\Delta T=\frac{PHI}{d},$$

where H is the magnetic field in gauss, I the current in absolute units, d the thickness of the plate in cm., and P the Ettingshausen coefficient.

The Hall and Ettingshausen effects are superposed, and unless the secondary electrodes in the Hall-effect determinations are made of the same material as the plate itself, the Ettingshausen temperature difference ΔT set up between the edges of the plate will result in a thermo-E.M.F. $\theta . \Delta T$ in the secondary circuit, where θ is the thermoelectric power of the electrode with respect to the

Graph IV.

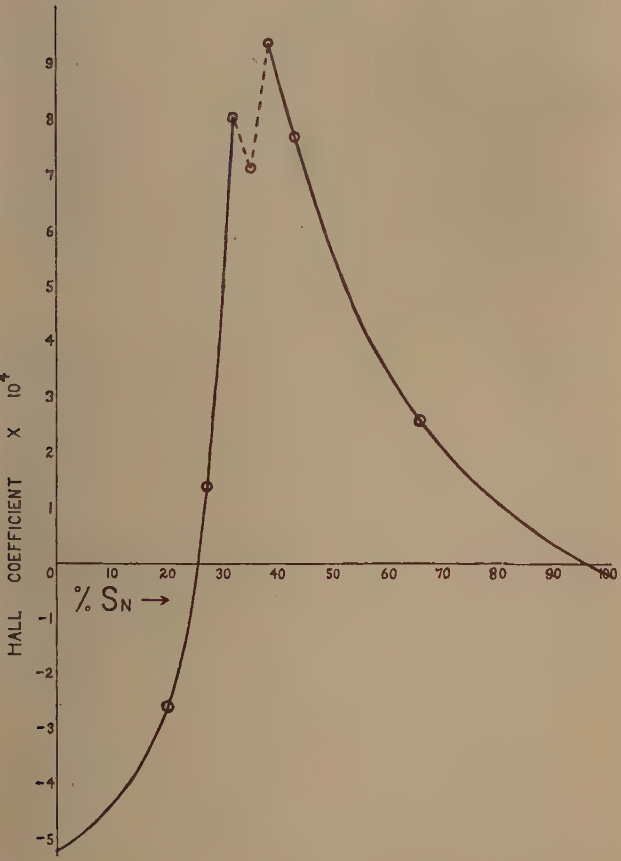


plate. Therefore the total potential difference as measured by the galvanometer in the Hall-effect determination is given by

$$E \doteq E_H \pm \theta . \Delta T,$$

where E_H is the true Hall P.D.

Then R, the Hall coefficient, becomes

$$R=\frac{E\times d}{H\times I}\pm P.\,\theta.$$

Generally the Ettingshausen coefficient P is very small, but the factor θ also determines whether a correction to the Hall coefficient is necessary. In the Hall-effect determinations, when the primary current is reversed with the galvanometer circuit closed, the deflexion representing the Hall E.M.F. is taken up in a few seconds, while the Ettingshausen thermo-E.M.F., if appreciable, produces a secondary deflexion. In the present experiments the electrodes were made of copper and no secondary deflexion was observed, and thus no corrections for the Ettingshausen effect have been made. The Hall coefficients have been determined within 1 per cent.

The Annealing of the Alloys.

The annealing temperatures were obtained from the equilibrium diagram given in the International Critical Tables, vol. ii. The chill-cast alloys were annealed in an electric furnace in an atmosphere of coal-gas, to prevent oxidation. One plate was annealed in nitrogen owing to the high annealing temperature. The furnace was heated to the required temperatures very slowly, and could be kept at these temperatures within a few degrees for long intervals of time. The annealing was usually performed in periods of about 8 hours, and the furnace was allowed to cool to room-temperature before removing the alloy. The process was repeated several times for each alloy. The temperatures at which the various alloys were annealed are given below :—

65·2 per cent. Sn,	34·8 per cent. Cu (SnCu) ...	155° C.
42·8 ,, ,, Sn,	57·2 ,, ,, Cu (Sn_2Cu_5)...	180° C.
38·4 ,, ,, Sn,	61·6 ,, ,, Cu ($SnCu_3$)...	565° C.
35·0 ,, ,, Sn,	65·0 ,, ,, Cu	
31·9 ,, ,, Sn,	68·1 ,, ,, Cu ($SnCu_4$) ...	
27·2 ,, ,, Sn,	72·8 ,, ,, Cu ($SnCu_5$)...	500° C.
20·0 ,, ,, Sn,	80·0 ,, ,, Cu	
10·0 ,, ,, Sn,	90·0 ,, ,, Cu	750° C.

The annealing of a plate of Cu_3Sn was also performed with the furnace evacuated to about 1/10 mm. pressure, and the result, as shown in Table I., is in good agreement with the plate annealed in coal-gas.

Discussion of Results.

The curves showing the relation between the electrical resistivity, temperature coefficient of electrical resistance, Hall effect, thermoelectric power, and the concentration of Sn in the alloy furnish singular points corresponding to both Cu_3Sn and Cu_4Sn. These curves differ greatly from the corresponding curves obtained for the copper-antimony alloys. The electrical resistivity, Hall effect, and thermoelectric power curves for the copper-antimony alloys * are similar in that the sign of the gradients of the curves is the same for corresponding compositions, but this is not the case with the curves for the copper-tin alloys.

The resistivity of the alloys of composition between 100 per cent. Sn and Cu_3Sn diminishes very gradually as the concentration of Sn is decreased. The resistivity of Cu_3Sn determined in the present experiments is $8\cdot72 \times 10^{-6}$ ohm, the value determined by Ledoux being $8\cdot75 \times 10^{-6}$ ohm. From Cu_3Sn to Cu_4Sn the resistivity increases rapidly to the value $47\cdot8 \times 10^{-6}$ ohm, while it diminishes in a regular manner as the composition is varied from Cu_4Sn to 100 per cent. Cu.

The curve showing the variation of the temperature coefficient of resistance with the concentration of Sn in the alloy is very sensitive to changes in composition of the alloy. The addition of tin to copper causes the temperature coefficient of resistance to diminish rapidly to a very low value. This low minimum value is constant over the range of composition from about 85 per cent. Cu, 15 per cent. Sn to Cu_4Sn, while between Cu_4Sn and Cu_3Sn the temperature coefficient of resistance increases very rapidly from the minimum value $5\cdot7 \times 10^{\ 4}$ to $35\cdot3 \times 10^{-4}$. As the composition of the alloy is varied from Cu_3Sn to 100 per cent. Sn, the temperature coefficient of resistance at first diminishes to a minimum value corresponding to an alloy of composition 54 per cent. Cu, 46 per cent. Sn, but afterwards increases uniformly. While singular points are obtained corresponding to the compounds Cu_3Sn and Cu_4Sn in the curve showing the variation of the temperature coefficient of resistance with the concentration of one metal in the alloy, no singular points are obtained corresponding to Cu_2Sb and Cu_3Sb † in the curve for the Cu-Sb system of alloys.

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* Stephens and Evans, *loc. cit.*

† Stephens and Evans, *loc. cit.*

While the crystal structures of Cu_3Sb and Cu_3Sn are similar, and possibly identical, the presence of the Sb or Sn atoms produces a remarkable change in the electrical properties of the structure. The resistivity of Cu_3Sb is about eleven times that of Cu_3Sn, but the temperature coefficient of resistance of Cu_3Sb is only one-eighth that of Cu_3Sn. It is interesting to note that in both the Cu-Sn and Cu-Sb series of alloys the compound with the low resistance has a high temperature coefficient of resistance, and that the compound with the greater content of copper has the greater resistance. Table V. gives the electrical properties of Cu_2Sb, Cu_3Sb, Cu_3Sn and Cu_4Sn.

TABLE V.

Compound.	Resistivity in microhms per cm.³ at 0° C.	Mean temp. coeff. of resistance between 0° and 100° C. × 10⁴.	Thermo-electric power with respect to Cu, in microvolts.	Hall coefficient.	Crystal structure.
Cu_2Sb......	10·4	39·6	− ·09	+·0013	Tetragonal $a_0=4·029$ Å.U. $C_0=6·140$ Å.U. Cell contains two molecules *.
Cu_3Sb......	98·5	4·33	+9·08	+·00176	Hexagonal close-packed, with the same axial ratio.
Cu_3Sn......	8·72	35·3	+ ·06	+·000935	
Cu_4Sn.....	47·8	5·72	−2·99	+·000802	Face-centred cube, with 416 atoms in unit cell.

* Howells and Jones (not yet published).

In the copper-antimony series of alloys the Hall effect and thermoelectric power vary in a similar manner as the composition is changed. In the copper-tin system, however, there is no similarity in form between the curves showing the variation of the Hall effect and thermoelectric power with composition of the alloy, although both curves show well-defined singular points corresponding to the compounds Cu_3Sn and Cu_4Sn. The points corresponding to the thermoelectric power of the alloys 57·2 per cent. Cu, 42·8 per cent Sn. and 34·8 per cent. Cu, 65·2 per cent. Sn do not lie on the curve. This may be due to the first alloy consisting of the Cu_3Sn and ϵ' phases, and the second of the ϵ' and ζ' phases.

Although the Hall effect for both copper and tin is negative, it is positive for all the alloys in the range of composition from about 74 per cent. Cu, 26 per cent. Sn to about 4 per cent. Cu, 96 per cent. Sn. This change in sign of the Hall effect seems to indicate that while the sign and magnitude of the effect may to some extent depend on the atom itself, it also depends to a great degree on the crystal structure of the metal or alloy. Cu_3Sn has the maximum positive Hall effect, and is about one-half that of Cu_3Sb. The Hall effect, which was examined for each alloy for magnetic fields up to 8000 gauss, was found to be independent of the magnetic field for all the alloys.

The magnetic susceptibilities of the copper-tin alloys have been examined by Clifford *. Although tin is slightly paramagnetic and copper is diamagnetic, the alloys formed by the addition of a small percentage of tin to copper are more diamagnetic than copper. A maximum is obtained corresponding to an alloy of composition near Cu_4Sn, and with an increase in the tin content the alloys become less diamagnetic. Only the alloys in a small range of composition near the tin end of the series are paramagnetic. It should be noted that the susceptibilities of copper and tin, $-1{\cdot}22\times10^{-6}$ and $+{\cdot}31\times10^{-6}$ respectively, given in this paper are not in agreement with modern values. A complete analysis of the magnetic susceptibilities of many series of alloys has been made by Honda and Endo †. Determinations were made at room-temperature and at about 50° C. above the melting-points of the alloys. These investigators concluded that intermetallic compounds existing in the solid phase up to the liquidus points also persist in the liquid phase. The susceptibility-concentration curve at room-temperature for the Cu-Sn alloys has a singular point corresponding to Cu_4Sn, with breaks in the curve corresponding to Cu_3Sn and CuSn. In the susceptibility-concentration curve of the melt, however, a minimum is obtained near 40 per cent. Sn. Both tin and all the Cu-Sn alloys at the high temperature are

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* Phys. Rev. vol. xxvi. no. 6 (1908).

† Journ. Inst. Metals, vol. xxxvii. p. 29 (1927).

diamagnetic. The susceptibility-concentration curve of the melt as obtained by Honda and Endo and the Hall coefficient-concentration curve obtained in the present experiments are similar in form, but the experimental results for the susceptibilities at room-temperature do not indicate any simple relation between magnetic susceptibility and Hall effect.

The effect of annealing on the resistivity of the alloys is shown in Table I. It is seen that the resistivity of one sample of the compound Cu_3Sn before annealing is approximately the same as that of pure Sn. The annealing of a plate of Cu_3Sn at 180° C. produced no appreciable change in the resistivity, but annealing at 565° C. diminished the resistivity by about 17 per cent. Annealing diminishes the resistivity of all the alloys of composition between Cu_3Sn and 100 per cent. Sn. The resistivity of the alloy 65 per cent. Cu. 35 per cent. Sn, which is between Cu_3Sn and Cu_4Sn, is increased by 35 per cent., and it seems that the alloys in the 6·5 per cent. range of composition from Cu_3Sn to Cu_4Sn are unstable. The resistivity of Cu_4Sn was only slightly diminished by annealing, but the resistivity of the 90 per cent. Cu, 10 per cent. Sn alloy, which consists of the α-phase, was increased by about 14·5 per cent. In the copper-antimony alloys, annealing increased the resistivity of the compound with the greater resistance, Cu_3Sb, while the resistivity of the other compound, Cu_2Sb, remained unchanged, but in the copper-tin alloys the compound with the greater resistance, Cu_4Sn, was not appreciably changed by annealing, while the resistivity of Cu_3Sn was diminished.

Summary.

1. The electrical resistivity, temperature coefficient of resistance, thermoelectric power, and Hall effect of the copper-tin series of alloys have been determined.

2. The alloys were chill cast in an iron mould in the form of plates, and the electrical resistivity at 0° C. was determined in this state. The resistivity was redetermined after the alloys were annealed at suitable temperatures, and the process of annealing was continued until the resistivity showed no further variation. The temperature coefficient of resistance, thermoelectric power, and Hall effect were then determined for the alloys in this final state.

3. Singular points corresponding to both Cu_3Sn and Cu_4Sn are obtained in each of the curves, showing the relation between electrical resistivity, temperature coefficient of electrical resistance, thermoelectric power, Hall effect, and the concentration of one metal in the alloy.

4. Although the Hall effect is negative for both copper and tin, it is positive for both the compounds Cu_3Sn and Cu_4Sn and the alloys of composition ranging between 74 per cent. Cu, 26 per cent. Sn and 4 per cent. Cu, 96 per cent. Sn. Cu_3Sn has the maximum positive Hall coefficient ·000935, which is approximately one-half the coefficient for Cu_3Sb.

5. Although the crystal structures of both Cu_3Sn and Cu_3Sb are hexagonal close-packed, with the same axial ratio, there is a remarkable difference in the electrical properties of these compounds. The resistivity of Cu_3Sb is about eleven times that of Cu_3Sn, but the temperature coefficient of resistance of Cu_3Sb is only one-eighth that of Cu_3Sn.

6. The effect of annealing on the resistivity of the alloys depends on their composition. A diminution is produced in the resistivity of Cu_3Cn, while the resistivity of Cu_4Sn remains practically unchanged.

In conclusion, I wish to express my warm thanks to Professor E. J. Evans, D.Sc., for his most valuable help and advice, and to Professor C. A. Edwards, D.Sc., who kindly granted facilities for preparing the alloys.

April 1929.

XXXV. *A New Conception of the Mechanism of Metallic Conduction.* *By* H. Monteagle Barlow, *Ph.D.*[*]

THE introduction of quantum mechanics into mathematical investigations of the mechanism of metallic conduction was facilitated by the previous existence of the classical theory. The latest developments initiated by

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[*] Communicated by the Author.

Sommerfeld [*] employ the idea of an electron gas interpenetrating the atoms of the metal as the basis of their argument.

In a recent paper [†] the author concluded that it is more accurate to regard the assembly of conduction electrons as forming what is equivalent to an incompressible fluid rather than a gas, and the following theory is put forward in an effort to provide a starting-point for future developments along these lines.

The Nature of the Conduction Process.

The atoms of the metal are regarded in the light of the Rutherford-Bohr model.

It is assumed that there are no " free " electrons in the sense that these are completely dissociated from the atoms. Every atom always has its normal complement of electrons, so that it can only give away one if at the same time it receives another.

Thus a current consists of a series of electrons passing simultaneously along a chain of atoms. In general the chain will have a zig-zag form, but with a resultant direction parallel with the electric force [‡].

The electrons concerned in the conduction process are supposed to reside in the outermost orbits of the atoms, and are recruited from the " valency " electrons employed in the theory of chemical action. It will be convenient to distinguish the particular electrons which lend themselves to the formation of an electric current by the name " fluid electrons."

If for any reason the outermost orbits of two neighbouring atoms were to come into contact, the nuclear attractions would exert opposing forces on a valency electron when situated between them, and such an electron would be equally ready to join the orbital system of either atom (fig. 1). A confluence of the outermost orbits is established at one point, and consequently no energy would be required to effect the transference of an electron from one atom to the other, provided that there occurred a simultaneous ejection of another similar electron by the receiving atom and absorption by the emitting atom.

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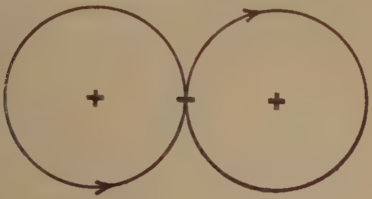
[*] Sommerfeld, *Naturwissenschaften*, Oct. 14, 1927, p. 63; and *Zeits. für Phys.* xlvii. pp. 1 & 43 (1928).

[†] Barlow, Phil. Mag. vii. p. 459 (1929).

[‡] This conception has been employed previously by (1) Fleming, 'The Interaction of Pure Scientific Research and Electrical Engineering Practice,' p. 38 (published by Constable, 1927); (2) Bridgman, Phys. Rev. xvii. p. 161 (1921), & xix. p. 114 (1922); and (3) Hall, Papers in Proc. Nat. Acad. Sci. and Phys. Rev.

The path of the electrons through the atoms themselves is supposed to be perfectly resistanceless, as required by Bohr's theory of non-radiating quantum orbits. Hence, in a pure metal at the absolute zero of temperature, when the atoms are presumably at rest, and always in contact, a current, once started, will go on indefinitely. If there were any appreciable opposition to the motion of an electron through the atoms one would expect this to account for a large part of the resistance of a conductor, and it seems unlikely that there would be such a marked change when the temperature is reduced.

Fig. 1.



Under ordinary conditions the heat-motions make it impossible to have a chain of atoms with their outermost orbits all in contact at the same time, so that the production of a current must then involve an expenditure of energy. The shape and size of the orbit to which an electron settles down in assuming a stationary state depends upon the proximity of the positive nucleus and other negative charges. The stability of the rotating electron with regard to displacements in the plane of its orbit is then determined by the constancy of the angular momentum. Measurements of atomic diameter and the Avogadro constant prove that the distance between neighbouring atoms of a mass of metal is very small, even at high temperatures, and it is therefore reasonable to suppose that the configuration of the orbits belonging to one atom of such an aggregation is profoundly influenced by the relative position of adjacent atoms. In fact the shape of the orbits must be continually changing to suit the conditions imposed at any instant by the heat-motions of the atoms.

Bohr assumes that the motions of the nuclei with respect to one another are so slow that the state of motion of the planetary electrons at any moment does not differ sensibly from that calculated on the assumption that the nuclei are at rest. This assumption is considered permissible on account of the large mass of the nuclei compared with that of the electrons, which means that vibrations resulting from a displacement of the nuclei are very slow compared with those resulting from a displacement of the electrons.

All available data point to the conclusion that at ordinary temperatures the valency electrons have an average velocity of vibration of about 10^6 or 10^7 cm. per sec., and consequently the orbits can scarcely be regarded as stationary states in the usual sense.

Energy must be expended to remove an electron from an atom, and, conversely, energy is radiated when a free electron is bound to an atom. In the process of transferring an electron from one atom to another not in absolute contact there must be a net absorption of energy. That energy ultimately appears as heat, and for the purpose of this discussion it is immaterial whether or not the energy takes some other form during the transition stage.

In order to get a mental picture of the mechanism adaptable to simple mathematical treatment we will suppose that the energy required to produce a current through a conductor is employed not in causing the electrons to jump through free space from one atom to another, but in distorting the outermost orbits until those belonging to adjacent atoms come together and allow an electron to pass across without opposition. This does not really involve any departure from the Bohr theory, because, as already pointed out, the shape of the orbits must be continually altering, and when an electron is transposed the change may be regarded as brought about either by a jump through free space from one stationary state to another or by a distortion of the orbits sufficient to bring them into contact at one point. The "fluid electrons" are therefore considered as always attached to one or other of the atoms which maintain electrical neutrality.

For a regular arrangement of the atoms there is obviously a relation between the spacing and the coefficient of expansion for the metal. As the temperature is raised from the absolute zero the atoms begin to execute heat-motions. and their average distance apart increases. Nevertheless there is generally one instant during each period of these heat-oscillations at which the outermost orbits of neighbouring atoms come together.

The application of an electromotive force to a metal bar is equivalent to an attempt to introduce some extraneous negative charges at one end and extract a similar number from the other end. As a result, the electron orbits belonging to the atoms at the two surfaces must suffer distortion, and that distortion will be propagated throughout the mass.

When a potential difference is maintained between two points on the conductor, it is known that a current will flow, no matter how small that potential difference, which is absorbed exactly by the forces opposing the flow of the current.

The outermost orbits of the atoms are assumed to be elongated in the direction of the pressure by an amount proportional to the pressure. This is in accordance with our knowledge of electric displacement in a dielectric, which we suppose only differs from a conductor in regard to the spacing of the atoms and the susceptibility of the atomic shell to distortion.

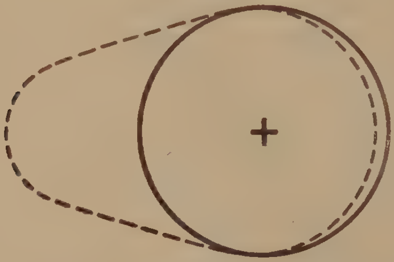
For a given potential difference between two points on a particular conductor there is a definite "total elongation" of the outermost electron orbits, remaining constant in time. That "total elongation" is really divided up between all the atoms separating the points considered, and is superposed on the heat-displacements. At one instant there may be no space between certain atoms, and therefore no distortion of their orbits is possible, but the remaining atoms in a particular chain will be allotted the elongation that the first-named are unable to accept.

In general the pressure is only sufficient to bridge a limited number of the gaps, so that the flow of "fluid electrons" is restricted to paths that are continually changing. The greater the applied pressure the larger the number of gaps included, and therefore the greater the average velocity of drift.

The distortion of an orbit is supposed to be perfectly elastic, the energy expended in producing a departure from the stationary state being completely returned if there is no interchange of electrons between different orbits. The linear relation between stress and strain for a metal bar subjected to a small tensile force indicates that an elastic deformation of the electron orbits is produced under such conditions.

A current in a conductor having a steady potential difference maintained between its ends is imagined to consist, therefore, of a number of rows of electrons periodically stepping forward along irregular chains of atoms. The electrons are always attempting to move towards the positive electrode, but they have to wait until an opportunity offers.

Fig. 2.



It might be argued that the compression of the orbit on one side of the atom counterbalances the extension on the opposite side, but when one considers that an inward displacement is opposed by the repulsion of all the electrons in the interior, whereas an outward displacement is only resisted by the comparatively weak residual attraction of the positive nucleus, it is apparent that there must be a net elongation of the atomic shell very nearly proportional to the applied force (fig. 2). This view is supported by the fact that the compression strength of a substance is invariably much greater than the tensile strength, although such a test is not altogether fair, on account of the accompanying lateral strain due to the molecules sliding over one another.

There is, of course, no reason to expect any change in the length of a conductor when a potential difference is established between its ends. The equivalent pressure on the electrons is always just balanced, so that forces of this nature can never tend to separate the atoms.

The production of heat by a current is also consistent with the mechanism we have been considering. The energy employed in forcing an orbital electron to take a different path from the normal must be converted into heat when that electron is transferred to a neighbouring atom. The process is analogous to what happens when a force which has been stretching a helical spring is suddenly removed. Oscillations are set up corresponding to the heat-motions of the atom. If, on the other hand, the force extending the spring is reduced to zero gradually, there will be no oscillations, and, in the case of an atom which is perfectly elastic, no energy loss.

The heat-content of the atom is supposed to be a property of the orbital electrons, the contribution of the positive nucleus being relatively negligible. The positive nucleus is so massive that it remains practically at rest, while its satellites oscillate in their orbits relatively to it. The vibrations of the electrons are very rapid, and the nucleus to which they are comparatively loosely held will not respond to such vibrations. The conditions may be compared with those prevailing when the upper end of a spiral spring supporting a heavy weight is given a simple harmonic motion of high frequency. The periodic time of the applied oscillation is so much smaller than that natural to the system that the weight is almost unaffected by the vibration.

In a conductor at uniform temperature the average kinetic energy of the atoms is constant; but, if a temperature gradient is maintained, the atoms at the hot end try to get more elbow-room than those at the cold end, so that the average compression of the outermost electron orbits under the forces of cohesion would have to vary from one point to another unless the atoms with the greater energy were given more space. Thus the hot atom compresses its cooler neighbour, tending to distort the electron orbits. That distortion is cumulative, and builds up along the temperature gradient towards the cold end. A convection current is set up to equalize the distribution of the heat, because more energy must be employed transferring electrons from one atom to another where the average distortion is large than where it is small.

Since every atom always has its normal number of electrons, the flow across any section must be the same in both directions.

If the orbit of an electron belonging to one atom is distorted, there is always a tendency to share that distortion with all the other atoms in the assembly. This is one of the most fundamental properties of a conductor, and has its origin in the closeness of the atoms and the ease with which their outermost orbits can be distorted. It is significant to compare the rate at which the E.M.F. is built up along the length of a conductor and a dielectric substance when the two lie side by side with a magnetic field sweeping across them *.

No matter how small the E.M.F. induced in an insulated conductor, the total displacement of electricity is the same, whether the conductor is made of copper or lead. In fact the displacement is not limited in any way by the atoms of the metal. Dielectrics are quite different. They are made up of bulky polyatomic molecules separated from one another by comparatively large distances. If the potential gradient is increased sufficiently, breakdown ultimately occurs, due to the fact that the "total elongation" of the electron orbits belonging to a chain of atoms between the electrodes becomes sufficient to bridge all the gaps. The conductivity exhibited by insulators when subjected to potential gradients less than that required to produce breakdown is probably caused by an absorbed electrolyte.

Before proceeding to consider how these ideas can be interpreted mathematically, it will be convenient to discuss one other factor which is of importance in determining the conductivity of a metal.

The normal positive valency is given by the number of electrons in the outermost orbit of the atoms. Thus, copper has a positive valency of one, zinc of two, aluminium three, and so on. The mechanism of conduction which we have been discussing only allows one electron at a time to cross the bridge between two atoms. Hence, with regard to the number of electrons available for the production of a current, there is no particular advantage in having more than one in the outermost orbit of each atom. On the other hand, the larger the number of valency electrons the more

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* H. A. Wilson, Phil. Trans. A, cciv. p. 121 (1905), and Proc. Roy. Soc. lxxiii. p. 490 (1904).

the work that has to be done to distort the orbit, and, consequently, the higher the resistance of the conductor. Moreover, a distortion of the outermost orbit involves a similar distortion of the inner orbits, so that the energy absorbed in this respect is also a function of the total number and distribution of planetary electrons in the atoms.

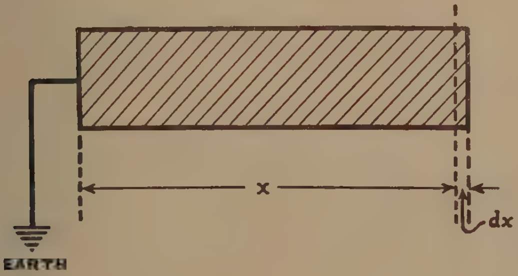
These deductions are confirmed by the periodic table of the elements. The electropositive metals with small atomic numbers are invariably the best conductors. Although the aluminium atom has three valency electrons, it only contains thirteen planetary electrons, and the resistance of this metal is therefore not very much greater than that of copper, with one valency electron and twenty-nine planetary electrons in the atom. Mercury and lead, with eighty and eighty-two planetary electrons in their atoms respectively, are relatively poor conductors.

Mathematical Interpretation.

(a) *Relation between potential and mechanical pressure on the "fluid" electrons.*

Consider a conductor of length x earthed at one end and raised to a potential V at the other (fig. 3). If the equivalent mechanical pressure per unit area on the electron fluid in the conductor is p, then the work done in producing a small displacement dx is given by

Fig. 3.



$$p \, . \, dx \text{ per unit area,}$$

and the corresponding quantity of electricity transferred from the end at potential V to earth is

$$N . e . dx \text{ per unit area,}$$

where N = number of "fluid" electrons per cubic cm. But by definition V = work done in moving unit charge from one end of the conductor to the other. Hence

$$V . N . e . dx = p . dx,$$

or $$p = VNe \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This relation is always applicable. It is equally true whether there is a flow of electricity or not. The pressure is exerted equally in all directions, as would be the case in an ordinary fluid.

(b) *Rate at which heat is developed in a conductor carrying current.*

Suppose that the average velocity of drift of the electron fluid through the conductor is w and the sectional area of the conductor is A, then the rate of doing work on the electron fluid is

$$pAw = VNeAw,$$

where V = P.D. between the ends of the conductor; but the current

$$I = NAew. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Hence power absorbed, producing heat in the conductor,

$$= VNeAw = IV,$$

as required.

(c) *Electrical conductivity and Ohm's Law.*

In considering the forces opposing the flow of the electron fluid through a conductor it is necessary to deal with time averages.

Let u = average velocity with which the distortion of an electron orbit is produced. This velocity is supposed to be practically constant over a wide range of temperature. Although the distortion of an orbit necessarily follows the heat-motion of the atomic shell, there are reasons to suppose that the fraction of the total mass of the atom in which the heat-energy is stored increases with the temperature. Thus at low temperatures (just above the point at which supra-conduction begins) the inner rings of electrons to which the positive nucleus is more firmly attached are practically at rest, so that the heat-energy of the atom is confined to the electrons in the outermost orbits. As the temperature is raised, the inner rings of electrons begin to absorb part of the thermal energy, and start oscillating about the positive nucleus in much the same way as the valency electrons.

Assuming equipartition of energy between degrees of freedom for the atoms, we find that at atmospheric temperature u should be of the order 10^6 cm. per sec.

Let f_1=average force required to distort an electron orbit sufficiently to effect the transfer of a single electron from one atom to the next. This operation is carried out with average velocity u.

Then, if f_2=average force opposing the flow of a single electron, with average velocity w, through the conductor as a whole, we have

$$\frac{f_1}{f_2}=\frac{u}{w}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Again, if l=length of the conductor, the average pressure on the electron fluid per unit area is given by

$$p=\mathrm{N}lf_2=\frac{\mathrm{N}lwf_1}{u}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

N being the number of "fluid electrons" per cubic cm., as before.

Consider a simple cubic lattice arrangement of the atoms. Let s=average spacing between two adjacent atoms. This spacing must be directly related to the amplitude of the heat-vibrations, and may be assumed proportional to the absolute temperature T[*].

Thus we have

$$s=y\mathrm{T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where y=increase in the linear dimensions of the average space occupied by a single atom per unit rise of temperature

Now let α=opposing force per unit outward displacement of the outermost electron orbit of an atom. This quantity is a function of the number and distribution of the electrons in the atom. It is quite independent of temperature. Hence

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[*] This hypothesis may not be strictly true, but the net result seems to be equivalent to it in most cases.

$$f_1 = \alpha s. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

From the preceding equations we have

$$p = \frac{\mathrm{N}l\alpha sw}{u} = \frac{\mathrm{N}l\alpha wy\mathrm{T}}{u}.$$

But $p = \mathrm{VN}e$ (eq. (1)),

$$\therefore \quad \mathrm{V} = \frac{p}{\mathrm{N}e} = \frac{l\alpha wy\mathrm{T}}{eu}$$

and $\mathrm{V} = \mathrm{IR} = \mathrm{NA}ew\mathrm{R}$,

where R = resistance of the conductor.

$$\therefore \quad \mathrm{R} = \frac{\mathrm{V}}{\mathrm{NA}ew} = \left[\frac{l\alpha wy\mathrm{T}}{eu}\right]\left[\frac{1}{\mathrm{NA}ew}\right],$$

that is,

$$\mathrm{R} = \frac{l\alpha y\mathrm{T}}{\mathrm{NA}e^2u}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This equation gives R, the dimensions of a velocity, as required.

The specific electrical conductivity is given by

$$\sigma = \frac{e^2\mathrm{N}u}{\alpha y\mathrm{T}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Thus, at constant temperature, σ is a constant, and Ohm's law is fulfilled. Moreover σ is inversely proportional to the absolute temperature, as required.

(d) *Thermal conductivity.*

When the temperature of a metal is increased it expands, because the atoms require more space in which to execute their heat-motions.

Let b = increase in the volume occupied by a single atom per degree rise in temperature.

Since an average of only one electron per atom is employed in producing a current in a conductor, we must have

$$\mathrm{N} = \begin{cases} \text{number of “ fluid electrons ” per cubic cm.} \\ \text{number of atoms per cubic cm.} \end{cases}$$

Consider a cube of metal whose sides are 1 cm. long at the absolute zero of temperature. When the temperature of this cube is raised to T degrees absolute, the volume increases by an amount

$$NbT,$$

N being in this case the number of atoms per cubic cm. If the cube were placed inside a box whose internal dimensions were 1 cm. each at all temperatures, the outward pressure which would be exerted on the sides of the box at the temperature T degrees absolute is given by

$$p'=GNbT, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where G=the bulk modulus of elasticity of the metal.

The kinetic theory gives a similar expression for the corresponding pressure exerted by a gas, that is,

$$p'=NKT.$$

K is a universal constant having the numerical value $1{\cdot}35\times10^{-16}$ ergs/degrees when p' is expressed in dynes per sq. cm. Thus the quantity K for a gas should be comparable with the quantity Gb for a solid.

Table I. shows that the quantity Gb is, in fact, very nearly constant for all metals, and has a value of about 10×10^{-16} ergs/degrees. The case of mercury is specially interesting because, when compared with the other metals, it has a small bulk modulus and a large coefficient of cubical expansion, but the value of Gb is about the same.

In a metal the pressure between the atoms due to their heat-motions is exerted for the most part on the electrons in the outermost orbits, because the inner orbits are relatively small *.

Thus it will not be far from the truth to take p' as the pressure on the " electron fluid " due to temperature, that is,

$$p'=p=GNbT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Now consider a section AB through a conductor in which a temperature gradient is maintained. Suppose that the section is taken between two layers of atoms, one of which is at temperature T_1 and the other at temperature T_2 (fig. 4.) The difference between the pressures exerted by the two layers is given by

$$p_1-p_2=GNb(T_1-T_2),$$

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* Frenkel, Phil. Mag. xxxiii. p. 297 (1917). Millikan, Phys. Rev. x. p. 194 (1917).

and since the velocity with which this resultant pressure causes the "fluid electrons" to flow across the section is u, the rate at which energy is transferred across the section is given by

$$(p_1-p_2)u=\mathrm{GN}bu(\mathrm{T}_1-\mathrm{T}_2).$$

If the diameter of an undistorted atom is d, the average temperature gradient is

$$\left[\frac{\mathrm{T}_1-\mathrm{T}_2}{d+s}\right] \quad \text{or} \quad \left[\frac{\mathrm{T}_1-\mathrm{T}_2}{d}\right] \quad \text{very nearly,}$$

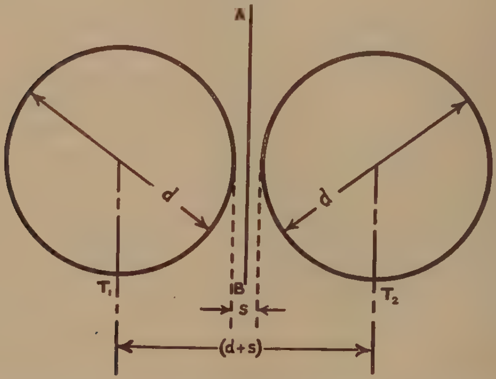
since s is small compared with d. Hence for a thermal conductivity λ we have

$$\lambda\left[\frac{\mathrm{T}_1-\mathrm{T}_2}{d}\right]=\mathrm{GN}bu[\mathrm{T}_1-\mathrm{T}_2]$$

and

$$\lambda=\mathrm{GN}bud. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Fig. 4.



But the coefficient of cubical expansion for a metal is three times the coefficient of linear expansion, and therefore

$$\mathrm{N}b=3\left[\frac{y}{d}\right] \quad \text{or} \quad \mathrm{N}bd=3y. \quad . \quad . \quad . \quad (12)$$

Hence

$$\lambda=3\mathrm{G}yu. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

(*e*) *Relation between thermal and electrical conductivity.*

We have now shown that the electrical conductivity

$$\sigma=\frac{e^2\mathrm{N}u}{\alpha y\mathrm{T}} \quad \text{(eq. (8)),}$$

and the thermal conductivity

$$\lambda = 3\mathrm{G}yu \text{ (eq. (13))},$$

Thus

$$\frac{\lambda}{\sigma} = \left[\frac{3\mathrm{G}y^2\alpha}{e^2\mathrm{N}}\right]\mathrm{T} = \beta\mathrm{T} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

This ratio is directly proportional to the absolute temperature as required by experiment. In order to satisfy the law of Wiedemann and Franz the quantity

$$\beta = \left[\frac{3\mathrm{G}y^2\alpha}{e^2\mathrm{N}}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

should have approximately the same numerical value for all metals. To prove this it is necessary first to determine α. The elastic constants of the metal provide some useful information regarding this quantity.

When a metal rod is subjected to a small longitudinal tensile force we may suppose that each atom undergoes an elastic extension. Taking two adjacent atoms, the force resisting such an extension is exerted presumably between the positive nucleus of the one and the planetary electrons of the other. A certain fraction z of the total interatomic force comes on the electrons in the outermost orbits, for which the restoring force per unit displacement is α.

Hence, if E = modulus of longitudinal elasticity of the metal, it is easy to show that

$$\alpha = z\left[\frac{\mathrm{E}}{\sqrt[3]{\mathrm{N}}}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

There are reasons to suppose that z is approximately the same for all common metals, having a value of about $\frac{1}{5}$, and in the subsequent calculations that assumption is made.

α has been calculated from the above formula, eq. (16), and the Wiedemann-Franz constant β deduced from eq. (15). The results are given in Table I., together with the corresponding values of the quantity u, which represents the average velocity of distortion of the outermost electron orbits. The agreement with experiment is remarkable considering the approximations introduced into the theory and the diverse sources from which the numerical values have been obtained.

There is, of course, no difficulty with the atomic heats, since there are no " free " electrons.

TABLE I.

Metal.	Values of Gb.	Values of α from $\frac{1}{5}\left[\frac{E}{\sqrt[3]{N}}\right]$ dynes per cm.	Values of the Wiedemann-Franz constant $\mathfrak{Z}$.		Values of u, cm. per sec.
			From experiment.	From $\frac{3Gy^2\alpha}{e^2N}$.	
Aluminium	$10{\cdot}0\times10^{-16}$	$3{\cdot}5\times10^{3}$	$2{\cdot}18\times10^{8}$	$2{\cdot}4\times10^{8}$	$13{\cdot}2\times10^{6}$
Iron	$10{\cdot}8\times10^{-16}$	$9{\cdot}7\times10^{3}$	$2{\cdot}78\times10^{8}$	$2{\cdot}5\times10^{8}$	$3{\cdot}2\times10^{6}$
Nickel......	$11{\cdot}2\times10^{-16}$	$9{\cdot}0\times10^{3}$	$2{\cdot}4\times10^{8}$	$2{\cdot}3\times10^{8}$	$2{\cdot}6\times10^{6}$
Copper ...	$10{\cdot}9\times10^{-16}$	$7{\cdot}1\times10^{3}$	$2{\cdot}3\times10^{8}$	$2{\cdot}7\times10^{8}$	$17{\cdot}6\times10^{6}$
Zinc	$9{\cdot}1\times10^{-16}$	$6{\cdot}0\times10^{3}$	$2{\cdot}31\times10^{8}$	$3{\cdot}8\times10^{8}$	$7{\cdot}3\times10^{6}$
Silver	$11{\cdot}3\times10^{-16}$	$4{\cdot}1\times10^{3}$	$2{\cdot}35\times10^{8}$	$2{\cdot}3\times10^{8}$	23×10^{6}
Cadmium .	$10{\cdot}0\times10^{-16}$	$2{\cdot}8\times10^{3}$	$2{\cdot}43\times10^{8}$	$2{\cdot}5\times10^{8}$	$7{\cdot}1\times10^{6}$
Tin	$10{\cdot}2\times10^{-16}$	$3{\cdot}2\times10^{3}$	$2{\cdot}53\times10^{8}$	$2{\cdot}5\times10^{8}$	$5{\cdot}6\times10^{6}$
Platinum..	$11{\cdot}5\times10^{-16}$	$8{\cdot}5\times10^{3}$	$2{\cdot}59\times10^{8}$	$2{\cdot}1\times10^{8}$	$3{\cdot}5\times10^{6}$
Gold	$11{\cdot}5\times10^{-16}$	$4{\cdot}5\times10^{3}$	$2{\cdot}44\times10^{8}$	$2{\cdot}0\times10^{8}$	$16{\cdot}8\times10^{6}$
Lead	$11{\cdot}0\times10^{-16}$	$1{\cdot}2\times10^{3}$	$2{\cdot}46\times10^{8}$	$1{\cdot}3\times10^{8}$	$2{\cdot}9\times10^{6}$
Mercury ...	$11{\cdot}3\times10^{-16}$	—	—	—	—

In conclusion the author desires to thank Sir Ambrose Fleming, D.Sc., F.R.S., for the help he has given and the interest he has taken in the development of this work.

University College, London.
March 1929.

XXXVI. *An Experimental Method for the Determination of the Ballistic Demagnetization Factor.* *By* DONALD FOSTER *.

ABSTRACT.

A METHOD is described for experimentally determining the ballistic demagnetization factor. By means of a double search coil of novel design the magnetization and the magnetic field intensity are determined from ballistic galvanometer deflexions. While the discussion refers mainly to circular cylinders, the scheme is adaptable to specimens of other shapes. It is particularly designed to obtain

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* Communicated by the Author.

accurate measurements of field intensity in cylinders of small diameter.

Details of a special design are given.

Curves are given which illustrate the variation of the demagnetization factor with the magnetization, as well as the dependence of this relation on the material and on the dimensional ratio.

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1. *Introduction.*

THE magnetic field intensity in a substance is the resultant of the externally applied field and that due to the magnetization of the substance. The latter component is called the demagnetizing field because it is directed in the opposite sense to the polarization which causes it. If H is the resultant field, H_0 the applied uniform field, and h the demagnetizing field, the vector equation is

$$H = H_0 + h.$$

In order that the result of measurements of the relation between the magnetization and the field intensity may be independent of the exterior form of the specimen, it is necessary either to calculate or to measure the quantity h. The determination of the demagnetizing field has long been a problem of great urgency and practical difficulty.

It has been shown that the magnetization is uniform only when the bounding surface of the material is of the second degree*. The ellipsoid is the only such surface which is finite. For this case the demagnetizing field is calculable. The thin ring may also be mentioned as a shape for which the magnetization is approximately uniform, and for which the demagnetizing field vanishes. For ellipsoids h is proportional to the magnetization I. The ratio $N = -\frac{h}{I}$, which is known as the demagnetization factor, depends only on the axial ratio of the ellipsoid. Unfortunately, however, these shapes are often inconvenient or impossible to employ in magnetic measurements. For example, neither form is suitable for use with metallic single crystals.

The most convenient shape is usually the right circular cylinder. The problem of calculating its demagnetizing field is insoluble, except in special cases, because the distribution of magnetization in a cylinder is dependent upon the magnetization curve of the material of which it is composed. A variety of apparatus has been developed for the purpose of obtaining uniform magnetization in cylinders in order to neutralize or render calculable the demagnetizing field. These devices are seriously limited in their accuracy and range of applicability. Permeameters of the yoke type have the additional disadvantage of putting the sample under constraint, and have been found unreliable when used with small stress-sensitive samples.

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* Neumann, J., Crelle's Journal, xxxvii. pp. 21–50 (1848). Maxwell, 'Electricity and Magnetism,' § 437.

It has been commonly supposed that N is a constant for circular cylinders of given dimensions. Tables based on this assumption have been prepared by DuBois * and others †, and are still in general use for calculating the demagnetizing field, although the serious limitations of the data have been pointed out. Lamb ‡ and Holborn § measured the distribution of magnetization in cylinders and found that, in iron, the centroids of free magnetism move toward the middle of the rod and then outward again as the magnetization is increased. Searle and Bedford ‖ using a magnetometric method measured h at the middle of a long iron wire. The magnetization was measured ballistically at the middle of the wire. They found that h is a maximum at about the value of I for which $\mu=\mu_{\text{max.}}$. This result is in agreement with the data of Lamb and of Holborn. It was also found that h exhibited hysteresis toward H and I. This fact is invoked to explain the occurrence, with the method of reversals, of values of h less than that corresponding to uniform magnetization. Recently Dussler ¶, by a ballistic method, has demonstrated that N as a function of I is dependent upon the material of which the cylinder is composed.

The middle of the axis of a cylinder is a critical point at which I is a maximum and N a minimum. N for this point has been called the ballistic demagnetization factor, since in

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* DuBois, H., 'Magnetische Kreise,' Berlin, p. 45 (1894); Wied. *Ann.* xlvi. p. 497 (1892).

† Ascoli, M. and Lori, F., *Atti della reale Accademia dei Lincei*, (5) iii. (2) p. 190 (1894). Mann, C. R., *Diss.* Berlin (1895); Phys. Rev. iii. pp. 359-369 (1896). Benedicks, C., *Ann. der Physik*, vi. p. 726 (1901). Schuddemagen, C. L. B., Phys. Rev. xxxi. p. 165 (1910).

‡ Lamb, C. G., Proc. Phys. Soc. Lond. xvi. pp. 509-518 (1899); Phil. Mag. (5) xlviii. pp. 262-271 (1899).

§ Holborn, L., *Sitz. der königl. preuss. Akad. der Wiss.* Berlin, i.-ii. pp. 159-168 (1898).

‖ Searle, G. F. C., and Bedford, T. G., Phil. Trans. Roy. Soc. Lond. A, cxcviii. pp. 33-104 (1902).

¶ Dussler, E., *Ann. der Physik*, lxxxvi. pp. 66-94 (1928).

ballistic measurements I is usually measured over a short segment at the middle of the sample.

Consideration of the facts shows that the ballistic demagnetization factor must be determined experimentally, point by point, along the magnetization or hysteresis curve of each specimen. It is the purpose of this paper to describe a convenient method whereby this may be accomplished.

2. *The Method of Measurement.*

The experimental arrangement is similar to that which is ordinarily used in making magnetic measurements ballistically. The sample is placed centrally in a magnetizing solenoid which provides a sufficiently uniform applied field. The double search coil is mounted inside the magnetizing coil and serves to measure both the magnetization and the field intensity. It consists of two coaxial solenoidal windings having equal numbers of turns. One coil is mounted inside the other, and the inner coil is wound on a radius just large enough to allow the pair of coils to be slipped over the specimen. When the coils are connected in series aiding to a ballistic galvanometer, the galvanometer deflexion can be made proportional to the magnetization I. When connected in series opposing, the effect due to magnetization is balanced out; and the galvanometer deflexion is proportional to the field H. By the use of an auxiliary air-core transformer, the double coil may be made to give deflexions proportional to the demagnetizing field h.

The method for measuring the field intensity is novel, chiefly in the design of the search-coil, which makes use of all the available area around the cylinder and introduces a minimum of electrical resistance, thus giving a sensitivity with rods of small diameter which has not been attained by other means.

The foundation of the method is the fact that the tangential component of magnetic intensity is continuous at the boundary between two media. The field intensity is measured in the region adjacent to the surface at the middle of the cylinder. While, in a uniform rod, the normal component vanishes at the middle, the method is independent of this condition because the measured quantities are the components of I and H parallel to the axis of the cylinder.

3. *Theory of the Double Secondary Coil.*

Let Φ be the flux linkage of the complete search-coil, and let a_1 be the effective area, and n_1 the number of turns on the inner coil, and a_2, n_2 the corresponding quantities for the outer coil. Let a_s designate the cross-sectional area of the sample. Then for series opposing

$$\Phi=\{(\mu-1)\mathrm{H}a_s+\mathrm{H}a_1\}(-n_1)+\{(\mu-1)\mathrm{H}a_s+\mathrm{H}a_2\}n_2$$
$$=(\mu-1)\mathrm{H}a_s(n_2-n_1)+\mathrm{H}(a_2n_2-a_1n_1).$$

Putting $\quad n_1=n_2\equiv n, \quad a_2-a_1\equiv a,$

$$\Phi=\mathrm{H}n(a_2-a_1)=\mathrm{H}na \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In series aiding connexion, we have

$$\Phi=(\mu-1)\mathrm{H}a_s(n_2+n_1)+\mathrm{H}(a_2n_2+a_1n_1).$$

If $\quad n_1=n_2\equiv n,$

$$\Phi=2(\mu-1)\mathrm{H}a_sn+\mathrm{H}n(a_1+a_2)$$
$$=8\pi a_sn\mathrm{I}+\mathrm{H}n(a_1+a_2).$$

If the term $\mathrm{H}n(a_1+a_2)$ is balanced out by an air-core transformer whose primary is in series with the magnetizing solenoid,

$$\Phi=(8\pi a_sn)\mathrm{I}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

When it is desired to measure the demagnetizing field directly, instead of the resultant field (equation 1), the balancing circuit may be set to give no deflexion when there is no sample in the search-coil. The equation for the series opposing connexion then becomes in effect

$$\Phi=\mathrm{H}na-\mathrm{H}_0na$$

(the second term being due to the transformer). Putting $\mathrm{H}=\mathrm{H}_0-\mathrm{NI}$,

$$\left.\begin{array}{l}\Phi=(\mathrm{H}_0-\mathrm{NI})na-\mathrm{H}_0na, \\ \Phi=-\mathrm{NI}na.\end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It is important in making the coils to consider the relative error in measuring H which is contributed by a given error in making n_1 equal to n_2. We have for series opposition

$$\Phi=(\mu-1)\mathrm{H}a_s(n_2-n_1)+\mathrm{H}(a_2n_2-a_1n_1).$$

Putting $\quad n_2-n_1\equiv\epsilon\,; \quad \frac{a_2}{a_s}\equiv\alpha\,; \quad \frac{a_1}{a_s}\equiv\beta\,;$

$$\Phi=a_s\mathrm{H}[\{(\mu-1)+\beta\}\epsilon+n_2(\alpha-\beta)].$$

When $\epsilon=0$,

$$\Phi=a_s\mathrm{H}n_2(\alpha-\beta).$$

The relative error in measuring H is therefore

$$\left\{\frac{\mu+\beta-1}{\alpha-\beta}\right\}\left(\frac{\epsilon}{n_2}\right);$$

and the factor $\frac{\epsilon}{n_2}$ is the relative error in making n_1 equal to n_2.

The quantity β is small, and μ is usually much greater than unity, so that the relative error reduces approximately to

$$\frac{\mu}{\alpha-\beta}\frac{\epsilon}{n_2}$$

which is proportional to the permeability. As a numerical example, suppose that

$$a_2=0{\cdot}922 \text{ cm.}^2\,; \quad a_1=0{\cdot}0697 \text{ cm.}^2\,;$$

$$\mu=10{,}600\,; \quad n_2=2761\,; \quad a_s=0{\cdot}0081 \text{ cm.}^2.$$

Then $$\frac{\mu}{\alpha-\beta}=100\,;$$

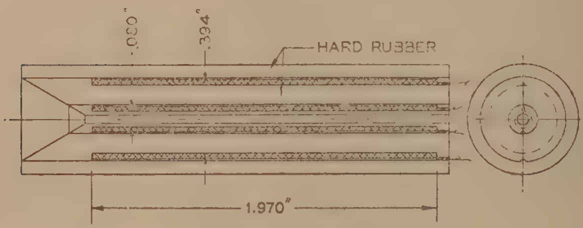
so that for an error in H of 1 per cent., the error in making the numbers of turns equal must be one-hundredth of 1 per cent. In this case, a tolerance of about one-third of a turn is allowed in matching the windings. It is necessary to avoid poor insulation or short-circuited turns in the coils. The existence of short circuits may be detected by means of an a.c. bridge, or by inserting into the search-coils a very long iron wire. As the magnetization approaches uniformity near saturation, the galvanometer deflexion due to the demagnetizing field becomes small in comparison with the effect of a single short-circuited turn, which may thus be readily detected.

4. *Design of the Coils and Measuring Circuit.*

Two facts determine the general design of the double search-coil. The polarization and the field intensity vary along the rod from the middle toward the ends; and the field intensity diminishes along the normal to the surface from the surface outward. These conditions are of such a nature as to limit the volume of the space in which the field is nearly uniform. The available winding volume is the quantity which determines the upper limit of sensitivity of the apparatus as a whole. When the winding volume of the search-coil is fixed, all sensitive moving-coil galvanometers give deflexions of about the same order of magnitude for a given change of flux. Using a given suspension fibre, the sensitivity of the galvanometer to voltage impulses increases as the field magnet is weakened or the number of turns on the moving coil is diminished. At the same time, however, the critical damping resistance of the galvanometer is diminished, and it is necessary to use fewer turns (in the same volume) on the search-coil in order to keep the galvanometer critically damped. The sensitivity of the circuit may be increased a little by using a coil whose resistance is greater than the critical damping resistance of the galvanometer. Usually, however, it will be found more convenient to operate the galvanometer critically damped.

Consideration of these limitations of ballistic galvanometers, when used to measure voltage impulses in a closed circuit, shows the importance of using a coil design which makes the best use of all the space around the middle of the specimen. This type of coil is particularly desirable for measurements on wires of diameter 0·1 cm. or less. If the cylinders to be measured have a small ratio of length to diameter, it will of course be necessary to use a short narrow coil. This does not imply a loss of accuracy in measuring the demagnetizing field because the field is much stronger for short specimens.

Fig. 1.



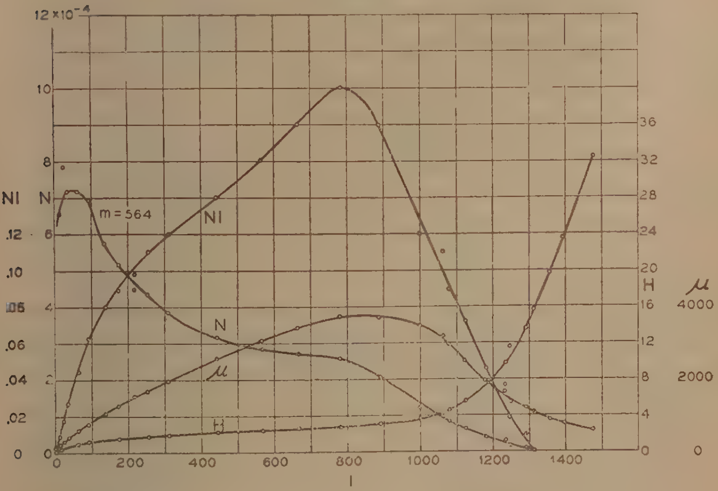
Double Secondary Coil.

A double coil which has been used for measurements on single crystal specimens of 0·1 cm. diameter has the dimensions shown in fig. 1. The windings have 2761·5 turns in each of No. 40 single silk-covered copper-wire. The inner and outer spools have resistances of 100 ohms and 357 ohms respectively, and this device gives a galvanometer deflexion of 1 mm. at 1 metre upon reversing a field of 0·08 gauss. The effective volume between the coils is about 4·3 c.c., yet they are small enough to operate in a sufficiently uniform field. They were designed for use with cylinders 60 cm. long and 0·05 cm. in radius. It is not possible to calculate the error due to the finite size of the coils except for the special case of uniform magnetization. In that case, it may be shown, for the example given above, that the extreme variation of the demagnetizing field within the coil is about 1 per cent. The average value, as measured by the coil, must therefore differ from the value at the middle of the sample by less than this amount.

5. *Some Examples of Measurements.*

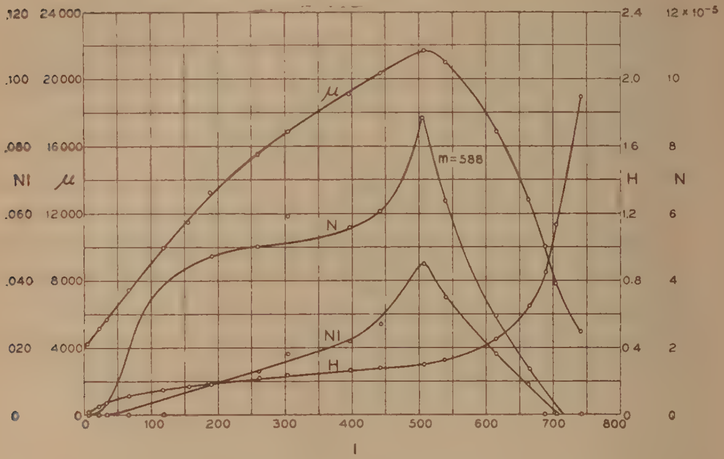
Typical data for well-annealed iron and permalloy wires of approximately 0·1 cm diameter are given in the following curves. The method of reversals was used, and the usual precautions were taken with regard to compensation of the earth's field, demagnetization of the sample, etc. In the figures m is the dimensional ratio (length/diam.). Fig. 2 shows the results for an electrolytic iron wire 57 cm. in length. Fig. 3 shows the same data for a permalloy (81 per cent. Ni, 19 per cent. Fe) wire of about the same dimensional ratio. The difference in the locations of the maxima of N is to be noted. It will be seen that for both materials the demagnetizing field is a maximum when the permeability is

Fig. 2.



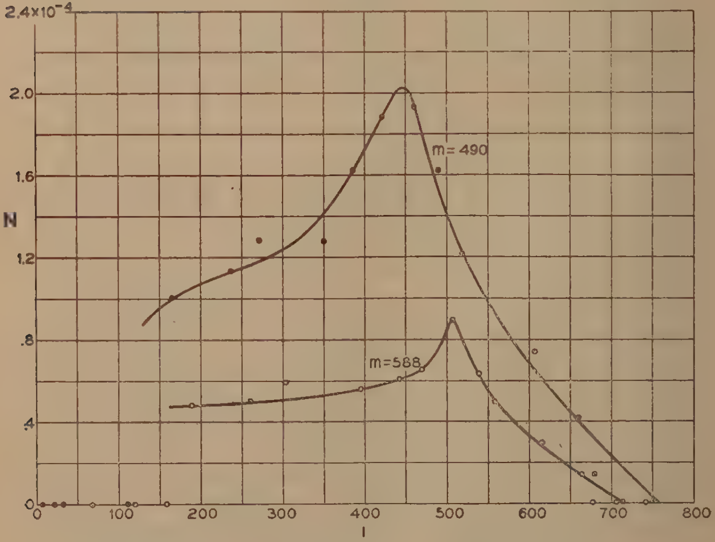
Electrolytic Iron.—Length = 57 cm.; diameter = 0·101 cm.

Fig. 3.



Permalloy.—Length = 60 cm.; diameter = 0·102 cm.

Fig. 4.



Permalloy.—Lengths 50 and 60 cm.; diameter 0·102 cm.

a maximum. For the permalloy samples N also has a maximum at the same point, although it occurs for a slightly lower value of I for the short permalloy specimen. Comparison of the demagnetization factors for two values of the dimensional ratio is given by fig. 4. The curves are taken on the same piece of permalloy.

In conclusion, it should perhaps be emphasized that the data given here apply only to the particular samples employed, and should not be used for the calculation of magnetic field intensities in other samples of the same dimensions.

I wish to express my thanks to Prof. L. W. McKeehan for stimulating my interest in this subject, and to Mr. Robert Bieling for assistance in preparing the data.

Bell Telephone Laboratories,
463 West St., New York, N.Y.,
October 1st, 1928.

XXXVII. *The Design of the Electron Collector for Retarding Voltage Analysis.* *By* H. W. B. SKINNER *and* S. H. PIPER, *University of Bristol**.

IN many experiments an electron collector (or Faraday Cylinder) is used to measure the current in an electron beam, and a velocity analysis of the beam is carried out by applying a variable retarding voltage so as to stop the slower electrons. If the slits which define the portion of the beam which is to be received are very narrow, probably there would be little difficulty in designing a suitable collector. We were requiring a collector with rather wide slits (2 by 6 mm.) and made one of the pattern shown in fig. 1. The outer case is a box of stainless steel sheet, $37 \times 19 \times 19$ mm. It was found on trial that this collector did not behave satisfactorily. The collector was mounted in a glass tube and a filament F (fig. 1) was placed in front of the first collector slit. The tube was exhausted, baked out at 420° C. for an hour, and sealed off from the pump. A charcoal tube, to be immersed in liquid air, was provided in order to absorb any gas given off.

A potential of 60 volts was applied between the filament F and the outer case C of the collector, and a variable voltage V was applied between C and the inner box B of the collector. A potential V which tends to stop electrons is taken as positive. The current to B was read by a galvanometer. Under these conditions one might hope, as V is gradually increased, to get no change in the galvanometer reading until V is nearly equal to 60 volts. The voltage-fall across the effective portion of the filament was only about ¼ volt, and so would cause very little round-off of the curve. The actual curve obtained is shown in fig. 4. There is a very large fall in the observed current as V passes through the value zero. It seems fairly clear that the true electron current is measured by the dotted straight line shown, and that the remaining current is spurious. For the quantitative analysis of a beam which contains electrons of various velocities it is essential to have a collector which, for each separate velocity, gives a flat retarding voltage curve. This condition is not satisfied by the collector described; an increase in the current for V negative would not matter, but the fall on the positive side of the zero is important.

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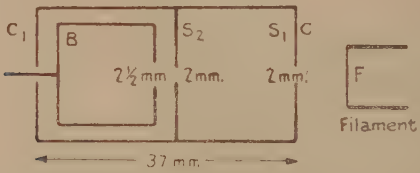
* Communicated by the Authors.

Fig. 1.



The most obvious probable causes of spurious effects in collectors are as follows:—

1. The increase in the current may be due to the secondary emission of slow electrons from the slits.
2. The penetration of the field of the collecting box through the rather wide slits may (*a*) focus or spread the electrons in the main beam so that more or less are collected, or (*b*) draw the slow secondaries into the collecting box.
3. Certain anomalies may be due to the emission of secondary electrons from the box itself.

We call the collector of fig. 1 C_1. In order to try to find out the cause of the spurious behaviour, and to make a collector which works better, we made up three more—collectors C_2, C_3, C_4 (figs 2 and 3). These collectors all had defining slits 2 mm. × 6 mm., and the outer cases of all were of the same dimensions. The collectors C_2 and C_3 had open-fronted collecting boxes, and were the same except that a close gauze of 1 mm. mesh was placed over the slit S_2 of the collector C_2. The collector C_4 was, as will be seen, similar to C_1, except that a fourth slit (the "screen") was placed between S_2 and the collecting box and was insulated from the system so that any voltage could be applied to it.

Fig. 2.

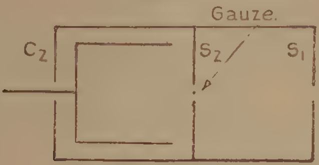
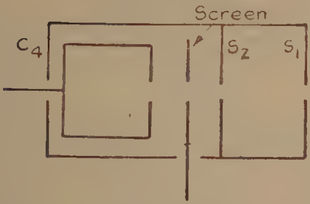


Fig. 3.



The slit on the screen was $2\frac{1}{2}$ mm. wide, so that very few electrons from the main beam could hit it.

Let us consider first the behaviour of the collectors C_2 and C_3. Their curves for 60-volt electrons are shown in figs 5 and 6. (In these, and all subsequent curves, we have plotted the points on such a scale that the "true" current has a standard value.) The most noticeable feature is the dip in the curves in the neighbourhood of 30 volts. It is clear that this is due to the cause (3) mentioned above, namely, the ejection of secondaries from the box itself. This shows that a closed collecting box is imperative.

It will also be noted that C_2 and C_3 do not show so large an increase in the current in the neighbourhood of $V=0$

as C_1 does. Further, that C_2, which had the gauze, shows a smaller increase than C_3. It is clear that the field penetration will be less in open collectors of the type of C_2 and C_3 than in closed collectors of the type of C_1. It is therefore certain that interpenetration of field plays a part in causing the current to rise when V becomes negative. For practical purposes this is unimportant, as we have stated. The fact that the rise occurs in this neighbourhood shows that it is due to the collection of relatively slow electrons, mostly ejected from the slit S_2. Some of these have sufficient energy to enter the box, even against a retarding voltage of 10–20 volts, and to this cause is due the practically important rise in the current as V is decreased from positive values to zero.

Fig. 4.

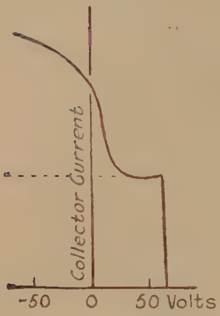


Fig. 5.

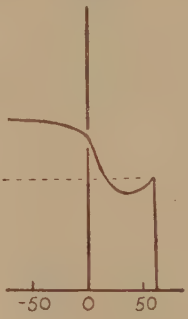


Fig. 6.

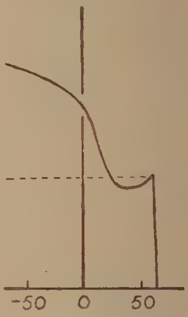


Fig. 7.

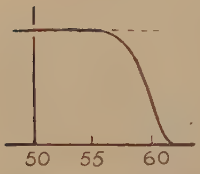


Fig. 8.

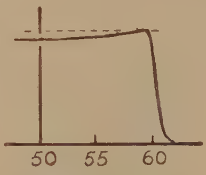
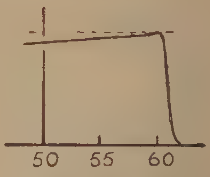


Fig. 9.



The feet of the curves for C_1, C_2, and C_3 are shown on a much larger voltage scale in figs. 7, 8 and 9. The zero of V was taken as the potential of the centre of the filament. The current into the collector came from a small part of the filament with a voltage drop across it of approximately $\frac{1}{4}$ volt. A slight spreading out of the feet of the curves will be caused by the finite velocity of emission of electrons from the filament. It is seen that for C_2 and C_3 the drop at $V=60$ is very sharp; for C_1 less so. The explanation of this is that penetration of the field from the collecting box through the slit S_2 causes a slight spreading of the main electron beam, and some of the electrons which, geometrically, should go into the box do not do so when they are nearly reduced to rest by the retarding voltage V. In the cases of collectors C_2 and C_3, where the field interpenetration is less, this effect is much less than for C_1. If a sharp foot to the collector curve is required we must take care to avoid the field interpenetration.

Fig. 10.

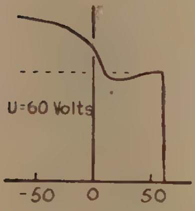


Fig. 11.

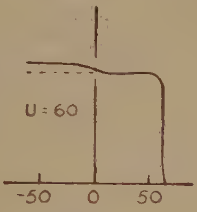


Fig. 12.

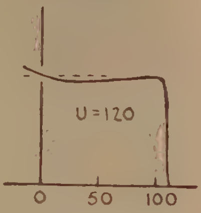


Fig. 13.

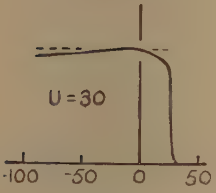


Fig. 14.

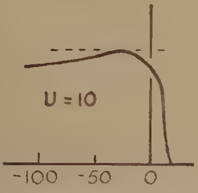
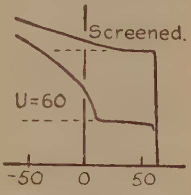


Fig. 15.



Actually in many cases this consideration is of little importance. An approximately flat curve from $V=60$ to $V=0$ may be required, and we hoped to obtain this by means of the screened collector C_4 (fig. 3). The screen can be used in a variety of ways, *e. g.*: (1) One may apply the retarding voltage to the screen and keep the box at a fixed potential. (This arrangment was a definite improvement, but the foot of the curve was excessively spread out on the voltage scale.) (2) One may place the screen at a high positive potential and hope that all the secondary electrons will be attracted to it, instead of going in the collecting box. Curves for this arrangement are shown in figs. 11, 12, 13, 14 (in which again the "true" current has been arbitrarily taken as a constant). They are taken for various voltages U between the filament and the case, as marked. The screen voltage (420 volts) was chosen as being suitable for electrons of velocity about 50–100 volts, and it is seen that for this range the curves are fairly flat from $V=0$ to $V=U$, and the foot is reasonably sharp. For the analysis of slow-speed electrons the screen voltage is too high, and the screen robs the collector of some of the electrons when V approaches the value U. All the same, the curves of figs. 11 to 14 show that, working with the screen at 420 volts, we could obtain reasonably accurate information about the relative numbers of electrons of velocities between 10 and 120 volts in a mixed beam, and this could not be done with the unscreened collector. If there are no fast electrons in the beam the screen voltage could profitably be diminished. A curve for $U=60$ with the screen at 60 volts is also shown in fig. 10. This shows, as might be expected, a similarity to the curve of fig. 4 for the collector C_1, and the advantage of using the screen at a high potential is apparent.

The curves for the various voltages V were taken with a constant current of $\frac{1}{2}$ m.a. between the filament and the case. The actual number of electrons collected was nearly independent of the accelerating voltage U, except in the 10-volt case*. One has, however, no certainty that the number of electrons passing through the slit S_1 is independent of V. If we place the screen at the same potential as the outer case of the collector, and choose the retarding voltage so that no stray electrons are collected, then we may obtain a measurement of the current through S_2. This may be called using the collector "unscreened." It was found that the collector current with 420 volts on the screen was in all cases very nearly twice what it was with the collector unscreened. A special test showed that this ratio was independent of the precise screen potential provided it were greater than about 300 volts.

The obvious interpretation of this ratio 2 is that it is due to a "suck in" of electrons through S_2, caused by field interpenetration. Some of the electrons, which in the absence of the screen would not pass through S_2, are deflected between S_1 and S_2, and go through into the collector. It was found, by experiments on the total filament emission, that the field penetration of the screen through S_1 was quite inappreciable. This "suck in" through the slit S_2 is a definite disadvantage of the screened collector. But the solid angle of the electron beam collected may be determined, and, as mentioned above, seems to be independent of the velocity, within wide limits.

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* The greater spread in the foot of the curve for 10 volts may be due to the fact that a higher filament temperature was used.

When there is gas in the tube, *e. g.*, by allowing the charcoal to warm up, experiments showed that the advantage of the screened collector was fully maintained. The curves for $U=60$ are given in fig. 15.

A property of the screened collector which may be very valuable in some cases is that, owing to the strong retarding field between S_2 and the screen, the collector will not pick up any positive ions in a mixed beam of electrons and positives.

We do not intend to advocate the use of the screened collector in all cases. The chief disadvantage of the ordinary unscreened collector is the rise in the current when the retarding voltage is approaching zero. Thus, suppose we have a beam of electrons of various velocities up to 60 volts. We reduce the retarding voltage to 10 volts and the current rises. We deduce that there are a number of 10-volt electrons in the beam. This deduction may be quite erroneous. In cases of this sort the screened collector is a definite improvement; its only disadvantage, beside the extra complication, is the "suck in." In experiments where the beam of electrons is known to be practically homogeneous, the screen is of no use. In these cases, if we require a fine analysis of the beam, our tests have shown that considerable care should be paid to the question of field interpenetration through the slits. The chief value of these experiments is to show the kind of error into which it is possible to fall, and to emphasise the importance of trying the working of a collector with a beam of electrons of homogeneous velocity.

Summary.

Various types of errors into which it is possible to fall in using an electron collector of the ordinary type are discussed; and a screened collector is described which, for some purposes, is a definite improvement on the usual type.

XXXVIII. *Preliminary Determinations of Standard Electrode Potentials in Methyl Alcohol.* By PHILIP STRACHAN BUCKLEY, *B.A.*, *B.Sc.*, *and* Sir HAROLD HARTLEY, *M.A.*, *F.R.S.*[*]

DETERMINATIONS of the standard electrode potentials of certain elements in methyl alcohol have been made by Neustadt and Abegg[†], Isgarischew[‡], Neustadt[§], and Carrara and Agostini[‖], but the values are known with much less certainty in this solvent than in water, as much of the experimental work has suffered from the following sources of error :—

(1) Insufficient attention was paid to preparing the solvent in a pure state.

(2) In the absence of any information as to the activities of the ions, the conductivity ratio $\frac{\lambda_c}{\lambda_0}$ was invariably used as a measure of their concentration.

(3) Calomel electrodes in water were used as reference standards. Besides the uncertainty of the liquid junction potential, this procedure introduces a risk of contaminating the solutions with water.

(4) Salts were used which do not behave as strong electrolytes in methyl alcohol, *e. g.*, the chlorides and nitrates of certain divalent metals.

(5) Sufficient care was not taken to prepare the metal electrodes in a reproducible and strainless condition.

(6) Liquid junction potentials were often ignored.

The values found by previous workers are given in Table I., referred in each case to silver, to which the value 0·76 volt is assigned, its approximate standard electrode potential in methyl alcohol referred to hydrogen as zero.

It will be seen that comparatively few elements have been investigated, and that the results of different investigators do not show satisfactory agreement.

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[*] Communicated by the Authors.

[†] *Zeit. Phys. Chem.* lxix. p. 486 (1909).

[‡] *Zeit. Elect.* xviii. p. 568 (1912), and xix. p. 491 (1913).

[§] *Zeit. Elect.* xvi. p. 866 (1910).

[‖] *Gazz. chim. ital.* xxxv. I. p. 132 (1905).

The present communication contains an account of a new series of determinations of these constants for certain uni- and divalent elements in methyl alcohol. The measurements were planned so as to avoid as far as possible the above-mentioned sources of error.

TABLE I.

	Neustadt & Abegg.	Isgarischew.	Neustadt.	Carrara & Agostini.
Zn	−0·78	−0·65	...	−0·67
Cd	...	−0·30	...	−0·31
Pb	−0.21			
Cu	+0·33	+0·27	...	+0·43
Hg	+0·72			
Ag	+0·76	+0·76	+0·76	+0·76
I	...	...	+0·48	
Br	...	...	+0·90	
Cl	...	...	+1·19	

EXPERIMENTAL PROCEDURE.

The potentiometer, thermostats, and method of shielding were the same as those used by Nonhebel and Hartley *, and the cells were made of durosil glass in the form described by them. All measurements were carried out at 25·0 ± ·02°C. The alcohol was prepared by the method described by Hartley and Raikes †. The salts used were pure specimens that had been prepared for conductivity work. The concentration of all solutions has been expressed in mols per 1000 grams of solvent, and accordingly molal activity coefficients have been used, referred to a standard state corresponding to the value of $E_0{}^m$ defined by the equation

$$E_0{}^m = E + 0{\cdot}1183 \log m\gamma,$$

as explained by Woolcock and Hartley ‡.

The standard electrode potential, indicated by the symbol E.P., is taken as the potential of an element in contact with a solution containing its ions at unit activity defined as above, when measured against an electrode of hydrogen at atmospheric pressure, in a methyl alcohol solution containing hydrogen ions at unit activity. The sign of the electrode

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* Phil. Mag. l. p. 729 (1925).

† J. Chem. Soc. cxxvii. p. 524 (1925).

‡ Phil. Mag. v. p. 1133 (1928).

potential is therefore in agreement with the usual custom adopted in Europe, but is the opposite of that used by G. N. Lewis. The values of the electromotive forces of the combinations described in this paper are written in accordance with the usual convention that the electrode on the right hand of the symbolic representation of the cell is positive.

LIQUID JUNCTION POTENTIALS.

Nearly all the cells investigated included one or more liquid junctions, and it was essential that the potential differences at these junctions could be evaluated. Attempts were first made to eliminate the potentials at the liquid junctions by the use of a bridge consisting of a suitable saturated salt solution. The cell

$$\mathrm{Ag, AgCl}\quad \begin{array}{c|c} \mathrm{HCl} & \mathrm{NaCl} \\ 0{\cdot}1\ \mathrm{m.} & 0{\cdot}1\ \mathrm{m.} \end{array}\quad \mathrm{AgCl, Ag}$$

gave an electromotive force of 20·6 mv., and on the assumption that the activity coefficients of sodium chloride and of hydrogen chloride are the same at this dilution, and that therefore the potentials at the two electrodes are equal and opposite, this value represents the potential difference at the liquid junction. When the side-tubes of the two half-cells dipped into a saturated solution of ammonium nitrate, an electromotive force of 12·6 mv. was obtained. The theoretical boundary potential calculated by means of the formula of Lewis and Sargent* was 20·2 mv., which is in good agreement with the observed value. A similar cell containing hundredth molal solutions showed an electromotive force of 17·85 mv. when the junctions were kept flowing, but the value rose to 17·95 mv. as the boundary aged. When the liquid junction was made by means of a saturated solution of ammonium nitrate, the electromotive force was 12·45 mv., whilst a saturated solution of potassium iodide gave a value of 4·35 mv. The value of the electromotive force at the junction calculated by the Lewis and Sargent formula is 17·9 mv., which agrees well with the observed value 17·85 mv. These results justify the assumption of the equality of the activity coefficients of sodium and hydrogen chlorides in dilute solution, and show that it is impossible to eliminate completely the liquid junction potentials in methyl alcohol by the use of a bridge of saturated salt solution. In addition, these two experiments show that the ordinary formulæ may be used to calculate liquid junction potentials in methyl alcohol with reasonable accuracy. In the present investigation the following formulæ have been employed for this purpose :—

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* J. Amer. Chem. Soc. xxxi. p. 363 (1909).

1. For the general case in which the two solutions contain electrolytes at concentrations c_1 and c_2, whose cations have respectively mobilities u_1 and u_2 and valencies w_1 and w_2, and whose anions have mobilities v_1 and v_2 and valencies w_1' and w_2', Henderson's * formula is

$$E=\frac{RT}{F}\cdot\frac{(u_1-v_1)c_1-(u_2-v_2)c_2}{(u_1w_1+v_1w_1')c_1-(u_2w_2+v_2w_2')c_2}\log_e\frac{(u_1w_1+v_1w_1')c_1}{(u_2w_2+v_2w_2')c_2}.$$

The following special cases are of importance.

(*a*) When the solutions contain the same uni-univalent salt at concentrations c_1 and c_2,

$$E=\frac{u-v}{u+v}\cdot\frac{RT}{F}\log_e\frac{c_1}{c_2}.$$

(*b*) When the solutions are of equal concentration and all the ions are univalent,

$$E=\frac{RT}{F}\cdot\frac{(u_1-u_2)-(v_1-v_2)}{(u_1-u_2)+(v_1-v_2)}\log_e\frac{(u_1+v_1)}{(u_2+v_2)}.$$

(*c*) If, in addition, they have a common ion,

$$E=\frac{RT}{F}\log_e\frac{\lambda_v}{\lambda_v'},$$

where λ_v and λ_v' are the equivalent conductivities of the two solutions.

(*d*) For equally concentrated solutions of salts having a common univalent anion combined with univalent and divalent cations, Henderson's equation reduces to

$$E=\frac{RT}{F}\cdot\frac{(u_1-u_2)}{(u_1-2u_2)}\log_e\frac{(u_1+v)}{(2u_2+v)}.$$

2. As a check on the results obtained for the potentials at liquid junctions comprising solutions of salts containing divalent ions, the independent formula of Pleijel † has also been employed. For the potential between equally concentrated solutions of salts $M'x$ and $M''x_2$ where M' has the

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* *Zeit. Phys. Chem.* lix. p. 118 (1907), and lxiii. p. 325 (1908).

† *Zeit. Phys. Chem.* lxxii. p. 33 (1910).

mobility u_1, M″ has the mobility u_2, and x has the mobility v, this gives

$$E = \frac{RT}{F} \cdot \frac{4u_2 - 3u_1 + v}{8u_2 - 3u_1 + v} \log_e \frac{4}{3} \frac{2u_2 + v}{u_1 + v}.$$

In the application of this formula and of Henderson's the "mobility" of a divalent ion is taken as its mobility divided by its valency.

The data required for these calculations were obtained from the paper of Frazer and Hartley * and from unpublished figures for ionic mobilities available in this laboratory. In addition, certain conductivity measurements were made, the results of which are shown in Table II.

Table II.

Salt.	Concentration in gram equivalents per 1000 gms. MeOH.	Equivalent conductivity.
NaCNS	0·02	80·75
KI	0·054	76·2
NaBr	0·1	60·25
$TlClO_4$	0·00986	101·8
$AgClO_4$	0·01	96·76
$NaClO_4$	0·01	92·88
$AgNO_3$	0·00875	76·32
NaCl	0·01	78·3
NaCl	0·1	55·74

The values for the equivalent conductivity of sodium chloride calculated from the data of Goldschmidt and Dahl † at 0·01 m. and 0·1 m. are 79·2 and 56·0 respectively.

Reference Electrodes.

Owing to the lack of a zero-electrode, constant and reproducible reference electrodes are indispensable to precise electromotive force measurements. In the present investigation, as is customary in water, the normal hydrogen electrode has been taken as the ultimate standard of reference. The hydrogen electrode in methyl alcohol is, however, unsuitable for use as a practical reference standard owing to the change of hydrion concentration due to esterification, to the considerable changes in the potential

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* Proc. Roy. Soc. cix. p. 351 (1925).

† *Zeit. Phys. Chem.* cxiv. p. 3 (1924).

produced by small amounts of water with which the solutions may become contaminated, and to the fact that the iridized gold electrode is easily poisoned, and in methyl alcohol soon loses its activity, so that a fresh one is frequently required.

A secondary reference standard is needed whose potential is accurately known in terms of the normal hydrogen electrode, and for this purpose electrolytic silver-silver chloride electrodes appear to be most suitable. For prolonged measurements, however, these have the disadvantage that they can be relied on for only one or two days, and it was found in practice more convenient to employ reference electrodes of a type that could be used over long periods, and to check their potentials at intervals against freshly-prepared electrolytic silver-silver chloride electrodes. Calomel electrodes and electrodes of granular silver and precipitated silver chloride in both tenth and hundredth molal sodium chloride solution have been used for this purpose. Great care must be taken if the silver-silver chloride electrodes are to give reproducible values, whilst the calomel electrodes show a slow, continuous drift. Their potential, measured against a silver-silver chloride electrode in a solution of sodium chloride of the same concentration, was initially 46·5 mv., and rose to 49·9 mv. after three months and to 51·5 mv. after five months. This drift would be explained if slow oxidation of the calomel were taking place, as suggested by Gerke * and by Randall and Young †.

ACTIVITY COEFFICIENTS.

Electromotive force measurements are practically the only means available for the determination of activities in this solvent, and for this purpose it is necessary to use electrodes reversible to both the ions of the electrolyte. Wolfenden, Wright, Ross-Kane, and Buckley ‡ failed to obtain activity coefficients for sodium chloride solutions using electrodes of sodium amalgam, and hydrogen is the only electrode reversible to the cation whose behaviour has been studied in methyl alcohol and found satisfactory. The activity coefficients of hydrogen chloride in this solvent have been determined by Nonhebel and Hartley §. In the absence of values for the activity coefficients of other electrolytes, salts have been chosen which are known, from a study of their

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* J. Amer. Chem. Soc. xliv. p. 1684 (1922).

† J. Amer. Chem. Soc. l. p. 989 (1928).

‡ Trans. Faraday Soc. xxiii. p. 491 (1927).

§ Phil. Mag. l. p. 729 (1925).

conductivities in methyl alcohol, to behave as strong electrolytes, and it has been assumed that the values of the activity coefficients of all uni-univalent electrolytes are the same as that of hydrogen chloride at the same concentration in dilute solution. This procedure is justified by the results of the two experiments described on p. 322, in which the assumption of similar activity coefficients for sodium chloride and hydrogen chloride led to values for the liquid junction potentials, which agreed closely with those calculated from the theoretical equation.

The activity coefficients of divalent ions were calculated by means of the equation of Debye and Hückel*,

$$-\log_e f_i = z_i^2 \frac{e^2 \, . \, K}{2 D k T} ;$$

where K is defined as

$$\sqrt{\frac{4\pi e^2}{DkT} \Sigma n_i z_i^2} ;$$

f_i is the activity coefficient of any ion, n_i the number of ions of the ith sort per c.c., and z_1 their valency, e the charge on an electron, k the Boltzmann gas constant, T the absolute temperature, and D the dielectric constant of the solvent. Inserting the numerical values of these constants,

$$e = 4{\cdot}77 \, . \, 10^{-10} \text{ E.S.U.}, \quad k = 1{\cdot}371 \, . \, 10^{-16} \text{ erg/degree, and}$$
$$D_{\text{MeOH}} = 30{\cdot}3,$$

the expression becomes, for a divalent ion,

$$-\log f_i = 2{\cdot}427 \sqrt{\Sigma n_i z_i^2}.$$

If the concentration of the solution is c mols per litre, and the anion is univalent,

$$-\log f_i = 5{\cdot}975 \sqrt{6c}.$$

It is important to notice that the activity coefficients calculated from this formula refer to concentrations expressed in mols per litre. However, in dilute solutions whose density does not differ appreciably from that of the pure solvent, the numerical values of f and of the molal activity coefficient γ defined on p. 321 are identical.

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* *Phys. Zeit.* xxi. p. 185 1923); xxv. p. 97 (1924).

EXPERIMENTAL RESULTS.

Hydrogen.

The data of Nonhebel and Hartley* for the electromotive force of the cell,

$$H_2 - HCl \text{ in } MeOH - AgCl, Ag,$$

were used to calculate the potential of the electrode Ag, AgCl 0·1 m. HCl referred to the standard hydrogen electrode, giving a value of +0·0711 volt. On the assumption that the activity coefficients of hydrogen chloride and of sodium chloride are the same in tenth molal solutions, all potentials measured against the secondary reference electrode Ag, AgCl 0·1 m. NaCl have been referred to the standard hydrogen electrode by adding to them 0·0711 volt.

Sodium.

The standard electrode potential of sodium was obtained from the data of Wolfenden, Wright, Ross-Kane, and Buckley† for the electromotive force of the cell

$$\text{Sodium amalgam} - NaCl \text{ in } MeOH - AgCl, Ag.$$

The electromotive force of the equivalent cell with a metallic sodium electrode was first calculated from the data of Richards and Conant‡. Then if E is the electromotive force of the cell

$$Na - NaCl \text{ in } MeOH - AgCl, Ag$$

with a solution of sodium chloride of molality m and activity coefficient γ, the standard electrode potential of sodium ($E.P._{Na}$) can be calculated from the equation

$$E.P._{Na} - 0·071 = -E + 0·05915 \log (0·1 \times 0·461)$$
$$-0·1183 \log m\gamma,$$

since the difference of potential between the electrodes Ag, AgCl 0·1 m. NaCl (in which solution sodium chloride has an activity coefficient of 0·461) and the standard hydrogen electrode is 0·071 volt.

Measurements in three of the more concentrated solutions, in which the behaviour of the amalgam electrode has not yet become abnormal, gave the following values:—

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* *Loc. cit.*

† *Loc. cit.*

‡ J. Amer. Chem. Soc. xliv. p. 601 (1922).

m.	γ.	E.	E.P.$_{Na}$.
0·01654	0·685	2·9490	−2·727
0·0568	0·525	2·9023	−2·730
0·0748	0·496	2·8886	−2·727

The mean value of E.P.$_{Na}$ is −2·728 volt.

Thallium.

The combination

Saturated thallium amalgam.	$TlClO_4$	$NaClO_4$	NaCl	NaCl Hg_2Cl_2, Hg
	0·00987 m.	0·01 m.	0·01 m.	0·1 m.
	−	+ +	− −	+

2·4 mv. 4·4 mv. 2·7 mv.

gave an electromotive force of 0·623 volt after subtracting 0·7 mv. to allow for the calculated potentials at the liquid junctions.

The thallium amalgam was made by warming small pieces of pure thallium metal with one and a half times their weight of distilled mercury. It was placed in a half-cell into which a platinum wire was sealed, and before being covered with the solution of thallium perchlorate it was washed repeatedly with oxygen-free alcohol to remove traces of oxide.

Assuming the activity coefficient of 0·00987 molal thallium perchlorate solution to be 0·746, and adding a correction of 2·6 mv. to allow for the difference of potential between thallium metal and its saturated amalgam (measured by Richards and Daniels*), the standard electrode potential becomes −0·499 volt referred to Hg, Hg_2Cl_2 0·1 m. NaCl, or −0·379 volt referred to the standard hydrogen electrode.

Silver.

The combination

Ag, AgCl	NaCl	$NaClO_4$	$AgClO_4$	Ag
	0·01 m.	0·01 m.	0·01 m.	
	−	+ +	−	

4·4 mv. 1·1 mv.

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* J. Amer. Chem. Soc. xli. p. 1732 (1919)

gave an electromotive force of 0·5210 volt after subtracting a correction of 3·3 mv. to allow for the potentials at the liquid junctions.

A variety of silver electrodes were used to avoid errors due to mechanical strain in the metal. Silver wires coated electrolytically with silver from potassium silver cyanide solution were unsatisfactory. The best results were obtained using granular silver prepared by mixing boiling solutions of silver nitrate and ammonium formate. The silver perchlorate was prepared by dissolving pure silver oxide in perchloric acid, evaporating to dryness, and recrystallizing from benzene.

If the activity coefficient of 0·01 m. silver perchlorate solution is 0·745, the standard electrode potential of silver referred to Ag, AgCl 0·01 m. NaCl is +0·6465, or +0·7646 referred to the standard hydrogen electrode. A separate experiment, using silver wire electrodes, gave a value of +0·762 for the standard electrode potential of silver. The most probable figure is +0·764 volt.

Two experiments using 0·00875 m. silver nitrate solution gave values of 0·760 and 0·756 volt for the standard potential with different types of electrodes. Silver nitrate is known to be partially associated in methyl alcohol, and this would explain the lower values.

Cadmium.

As observed by Isgarischew[*], it was found impossible to obtain a steady potential from a rod of cadmium dipping into the solution of a cadmium salt in methyl alcohol. The continuous fall of potential, which he attributed to passivity, occurs even with amalgamated electrodes, but can be prevented by bubbling hydrogen into the solution, and by this means the maximum uncertainty of measurement was reduced to 0·01 volt.

The combination

$$\begin{array}{cc|c|cc}
 & \mathrm{Cd(ClO_4)_2} & \mathrm{NaClO_4} & \mathrm{NaCl} & \\
\mathrm{Cd} & & & & \mathrm{AgCl,\ Ag} \\
 & 0\cdot01\ \mathrm{m.} & 0\cdot01\ \mathrm{m.} & 0\cdot01\ \mathrm{m.} & \\
 & \qquad + & - \qquad + & - & \\
\end{array}$$

$$3\cdot4\ \mathrm{mv.} \qquad\qquad 4\cdot4\ \mathrm{mv.}$$

[*] *Zeit. Elect.* xviii. p. 568 (1912) and xix. p. 491 (1913).

gave an electromotive force of 0·578 volt after adding a correction of 8 mv. to allow for the potentials at the liquid junctions.

The cadmium perchlorate solution was made by mixing equivalent amounts of methyl alcohol solutions of cadmium bromide and of silver perchlorate from a weight-burette. The hydrogen was generated by electrolysis of caustic soda solution saturated with baryta, and was freed from oxygen, dried, and saturated with methyl alcohol vapour before entering the cell. To obtain satisfactory results the rods of cadmium must be cleaned with 30 per cent. sulphuric acid, washed, and dried immediately before being used. When the electromotive force of the cell had become steady, the addition of a few drops of a solution of benzenesulphonic acid had only a very slight effect on the potential, showing that the cadmium rods were not acting as hydrogen electrodes, since in that case there would have been a considerable change in potential corresponding to the great change of hydrion concentration.

The activity coefficient of the cadmium ion in 0·01 molal cadmium perchlorate solution, calculated from the formula of Debye and Hückel, is 0·05, so that the standard electrode potential of cadmium is $-0·376$ volt referred to Ag, AgCl 0·01 m. NaCl, or $-0·258$ volt referred to the normal hydrogen electrode.

Copper.—The potential of a copper electrode, like cadmium, falls continuously when placed in contact with methyl alcohol solutions of its salts, but a steady electromotive force was obtained when a stream of hydrogen was bubbled through the solution. Various copper wires were used as electrodes, since the necessity for the hydrogen stream makes it inconvenient to use the metal in a finely divided state. When the electromotive force had become steady, addition of a small amount of acid showed that the copper was not acting as a hydrogen electrode, and, moreover, had this been so, the introduction of hydrogen would have produced a fall of potential and not a rise, as was invariably observed. To obtain a steady electromotive force it is essential that the copper should be cleaned immediately before putting it into the solution, and that the latter should be already saturated with hydrogen. The copper wires were cleaned most effectively with dilute sulphuric acid, followed by quick washing and drying. The copper perchlorate solutions were made by mixing equivalent amounts of methyl alcoholic solutions of copper chloride and of silver perchlorate. The solution was almost colourless, and remained so when a steady potential was obtained as a result of cleaning the copper and passing hydrogen through the solution continuously. Without these precautions the solution became green during the measurements.

The combination

$$\begin{array}{lcc|cc|cr} & \mathrm{NaCl} & & \mathrm{NaClO_4} & & \mathrm{Cu(ClO_4)_2} & \\ \mathrm{Hg, Hg_2Cl_2} & & & & & & \mathrm{Cu} \\ & 0\cdot01\ \mathrm{m.} & & 0\cdot01\ \mathrm{m.} & & 0\cdot0067\ \mathrm{m.} & \\ & - & & + & & & \\ & & \multicolumn{2}{c}{4\ \mathrm{mv.}} & \multicolumn{2}{c}{\mathrm{negligible}} & \end{array}$$

gave in three separate experiments electromotive forces of 0·480, 0·466, and 0·476 volt. The calomel reference electrode had a potential of 0·172 volt referred to the standard hydrogen electrode, and the calculated activity coefficient of copper perchlorate in the 0·0067 molal solution was 0·087. The corresponding values for the standard electrode potential of copper are 0·504, 0·490, and 0·500 volt.

In a fourth experiment, in which the solution was 0·00486 molal, the potential of the copper referred to the standard hydrogen electrode was 0·294 volt. At this concentration the calculated activity coefficient is 0·125, and hence the standard electrode potential of copper is 0·484 volt. The most probable value from the four experiments is +0·49 volt.

THE SOLUBILITIES OF THE SILVER HALIDES AND THE CALCULATION OF THE STANDARD ELECTRODE POTENTIALS OF THE HALOGENS.

Solubility product of Silver Chloride.

Since the electrode Ag, AgCl 0·1 m. HCl has a potential of 0·071 volt referred to the standard hydrogen electrode, the activity of silver ions in that solution can be found by substituting the values $E=0\cdot071$ and $E.P._{Ag}=0\cdot764$ in the equation

$$E=E.P._{Ag}+0\cdot05915\log a_{Ag},$$

giving

$$E=E.P._{Ag}+0\cdot05915\log a_{Ag},$$

giving a value of $1\cdot94\,.\,10^{-12}$. Since the hydrogen chloride was 0·1 molal with an activity coefficient of 0·461, the solubility product of silver chloride is

$$1\cdot94\,.\,10^{-12}\times0\cdot1\times0\cdot461$$

$$=8\cdot93\,.\,10^{-14}$$

when the concentrations of the ions are expressed in gm. equivs. per 1000 grams of alcohol. The solubility of silver chloride is therefore $3{\cdot}0 \,.\, 10^{-7}$ gm. equivs. per 1000 grams of alcohol, assuming that the activity coefficient is unity in so dilute a solution.

Solubility product of Silver Bromide.

The combination

$$\begin{array}{lc|cl} & \text{NaBr} & \text{NaCl} & \\ \text{Ag, AgBr} & & & \text{Hg}_2\text{Cl}_2\text{, Hg} \\ & 0{\cdot}1\text{ m.} & 0{\cdot}1\text{ m.} & \\ & + & - & \end{array}$$

2·0 mv.

gave an electromotive force of 0·1785 volt after adding 2·0 mv. to allow for the calculated potential at the liquid junction. The Hg, Hg_2Cl_2 0·1 m. NaCl electrode had a potential of 49·6 mv. positive to Ag, AgCl 0·1 m. NaCl, so that the potential of the silver-silver bromide electrode relative to the latter was $-0{\cdot}1290$ volt or $-0{\cdot}058$ relative to the standard hydrogen electrode. Substituting the values

$$E = -0{\cdot}058, \quad E.P._{Ag} = 0{\cdot}764$$

in the last equation, the activity of silver ions in the sodium bromide solution is found to be $1{\cdot}26 \,.\, 10^{-14}$, and the solubility product of silver bromide

$$1{\cdot}26 \,.\, 10^{-14} \times 0{\cdot}1 \times 0{\cdot}461$$
$$= 5{\cdot}8 \,.\, 10^{-16}.$$

The solubility of silver bromide is therefore

$2{\cdot}41 \,.\, 10^{-8}$ gm. equivs. per 1000 grams of alcohol.

Solubility product of Silver Iodide.

The combination

$$\begin{array}{lc|cl} & \text{KI} & \text{NaCl} & \\ \text{Ag, AgI} & & & \text{Hg}_2\text{Cl}_2\text{Hg,} \\ & 0{\cdot}054\text{ m.} & 0{\cdot}1\text{ m.} & \\ & - & + & \end{array}$$

0·6 mv.

using granular silver and precipitated silver iodide, gave an electromotive force of 0·3375 volt after correcting for the potential at the liquid junction. Silver-silver iodide electrodes prepared electrolytically gave an initial value agreeing approximately with this, but their potential fell rapidly, and secondary reactions appeared to be taking place. The calomel reference electrode against which the measurement was made was 44·0 mv. positive to Ag, AgCl, 0·1 m. NaCl, so that the potential of the silver-silver iodide electrode referred to this was $-0{\cdot}2935$ volt, and the silver ion activity in the potassium iodide solution was $2{\cdot}09 \,.\, 10^{-17}$. Assuming that 0·054 m. potassium iodide solution has an activity coefficient 0·53, the solubility product of silver iodide is $6{\cdot}0 \,.\, 10^{-19}$ and the solubility of silver iodide is

$7{\cdot}7 \,.\, 10^{-10}$ gm. equivs. per 1000 grams of alcohol.

Solubility product of Silver Thiocyanate.

The combination

$$\begin{array}{lc|c|cl}
 & \text{NaCNS} & \text{NaCl} & \text{NaCl} & \\
\text{Ag, AgCNS} & & & & \text{Hg}_2\text{Cl}_2\text{Hg}, \\
 & 0{\cdot}02\text{ m.} & 0{\cdot}02\text{ m.} & 0{\cdot}1\text{ m.} & \\
 & + & - \qquad - & + &
\end{array}$$

2·6 mv. 1·9 mv.

using granular silver and precipitated silver thiocyanate, gave an electromotive force rising from an initial value of 0·023 to 0·055 volt, at which it became constant on the fourth day. Silver-silver thiocyanate electrodes prepared electrolytically were neither constant nor reproducible. Since the calomel electrode was 0·046 volt positive to Ag, AgCl 0·1 m. NaCl, the potential of the silver-silver thiocyanate electrode referred to this was $-0{\cdot}0009$ volt, and hence the activity of silver ions in the thiocyanate solution was $1{\cdot}4 \,.\, 10^{-12}$. If the activity coefficient of 0·02 m. sodium thiocyanate solution is 0·664, the solubility product of silver thiocyanate is

$$1{\cdot}4 \,.\, 10^{-12} \times 0{\cdot}02 \times 0{\cdot}664$$
$$= 1{\cdot}8 \,.\, 10^{-14},$$

and the solubility of silver thiocyanate is

$1{\cdot}3 \,.\, 10^{-7}$ gm. equivs. per 1000 grams of alcohol.

Solubility product of Thallium Chloride.

The combination

$$\begin{array}{lc|cl}
\text{Saturated thallium} & \text{NaCl} & \text{NaCl} & \\
\text{amalgam} & 0{\cdot}01\text{ m.} & & \text{Hg}_2\text{Cl}_2\text{, Hg} \\
 & \text{saturated with} & 0{\cdot}1\text{ m.} & \\
 & \text{thallium chloride} & & \\
 & - & + &
\end{array}$$

2·7 mv.

gave an electromotive force of 0·639 volt after correcting for the potential at the liquid junction. Adding 0·049 volt for the potential of the calomel electrode referred to Ag, AgCl 0·1 m. NaCl, and subtracting 0·0025 volt to allow for the difference of potential between thallium metal and its saturated amalgam, the activity of thallium ions in the 0·01 m. sodium chloride solution is found to be $3{\cdot}9 \,.\, 10^{-3}$, and since the activity of chlorine ions is $0{\cdot}01 \,.\, 0{\cdot}745$, the ionic product of thallium chloride is $2{\cdot}9 \,.\, 10^{-5}$.

If the activity coefficient could be assumed to be unity, as with more insoluble salts, the solubility of thallium chloride would be $5{\cdot}4 \,.\, 10^{-3}$ gm. equivs. per 1000 grams of alcohol.

The solubility data that have been obtained are shown in Table III., where they are compared with the figures for water.

TABLE III.

Salt.	Solubility product in methyl alcohol.	Solubility in methyl alcohol (gram equiv. per 1000 grams).	Solubility in water (gram equiv. per 1000 grams).	$\frac{\text{Solubility in water.}}{\text{Solubility in alcohol.}}$
AgCl ...	$8{\cdot}9 \,.\, 10^{-14}$	$3{\cdot}0 \,.\, 10^{-7}$	$1{\cdot}3 \,.\, 10^{-5}$	43
AgBr ...	$5{\cdot}8 \,.\, 10^{-16}$	$2{\cdot}4 \,.\, 10^{-8}$	$7{\cdot}8 \,.\, 10^{-7}$	33
AgI	$6{\cdot}0 \,.\, 10^{-19}$	$7{\cdot}7 \,.\, 10^{-10}$	$1{\cdot}0 \,.\, 10^{-8}$	13
AgCNS .	$1{\cdot}8 \,.\, 10^{-14}$	$1{\cdot}3 \,.\, 10^{-7}$	$1{\cdot}2 \,.\, 10^{-6}$	9·2
TlCl ...	$2{\cdot}9 \,.\, 10^{-5}$	$5{\cdot}4 \,.\, 10^{-3}$	$1{\cdot}5 \,.\, 10^{-2}$	2·8

The values for the solubility products of silver chloride, bromide, and iodide obtained by Neustadt*, when recalculated in terms of molal concentrations, are $9{\cdot}5 \,.\, 10^{-14}$, $6{\cdot}4 \,.\, 10^{-16}$ and $9{\cdot}5 \,.\, 10^{-19}$, in fair agreement with the above results.

Standard Electrode Potential of Chlorine.

The standard electrode potential of chlorine was calculated from the solubility product of silver chloride by the following method :—

The electromotive force of the cell,

$$Ag-AgCl-Cl_2,$$

is a measure of the free-energy decrease in the reaction

$$Ag_{(solid)}+\tfrac{1}{2}Cl_{2(gas)}=AgCl_{(solid)},$$

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* *Loc. cit.*

and must be independent of the nature and concentration of the intermediate electrolyte. The electromotive force E of the above cell is given by the equation

$$-\mathrm{E} = \mathrm{E.P.}_{\mathrm{Ag}} - \mathrm{E.P.}_{\mathrm{Cl}} + \frac{\mathrm{RT}}{n\mathrm{F}}(\log_e a_{\mathrm{Ag}}. + \log_e a_{\mathrm{Cl}'})$$

$$= \mathrm{E.P.}_{\mathrm{Ag}} - \mathrm{E.P.}_{\mathrm{Cl}} + 0{\cdot}05915 \log \mathrm{L}_{\mathrm{AgCl}},$$

where $\mathrm{E.P.}_{\mathrm{Ag}}$ and $\mathrm{E.P.}_{\mathrm{Cl}}$ are the standard electrode potentials and $\mathrm{L}_{\mathrm{AgCl}}$ the solubility product of silver chloride in any particular solvent.

The value of E can be found by substituting in the equation the values for water, $\mathrm{E.P.}_{\mathrm{Ag}} = 0{\cdot}7995$, $\mathrm{E.P.}_{\mathrm{Cl}} = 1{\cdot}3594$, and $\mathrm{L}_{\mathrm{AgCl}} = 1{\cdot}8 \,.\, 10^{-10}$. E is thus found to be 1·135 volt, agreeing well with the directly observed value of Gerke *, 1·1362 volt.

Substituting now in the equation the values for methyl alcohol, $\mathrm{E.P.}_{\mathrm{Ag}} = 0{\cdot}764$ and $\mathrm{L}_{\mathrm{AgCl}} = 8{\cdot}93 \,.\, 10^{-14}$,

$$\mathrm{E.P.}_{\mathrm{Cl}} = +1{\cdot}128 \text{ volts.}$$

Standard Electrode Potential of Bromine.

The electromotive force of the cell,

$$\mathrm{Ag} - \mathrm{AgBr} - \mathrm{Br}_2,$$

is given by the equation

$$-\mathrm{E} = \mathrm{E.P.}_{\mathrm{Ag}} - \mathrm{E.P.}_{\mathrm{Br}} + 0{\cdot}05915 \log \mathrm{L}_{\mathrm{AgBr}}$$

By substituting the values for water, $\mathrm{E.P.}_{\mathrm{Ag}} = 0{\cdot}7995$, $\mathrm{E.P.}_{\mathrm{Br}} = 1{\cdot}0659$, and $\mathrm{L}_{\mathrm{AgBr}} = 6{\cdot}5 \,.\, 10^{-13}$, E is found to be +0·986 volt.

Substituting now in the equation

$$-0{\cdot}986 = \mathrm{E.P.}_{\mathrm{Ag}} - \mathrm{E.P.}_{\mathrm{Br}} + 0{\cdot}05915 \log \mathrm{L}_{\mathrm{AgBr}}$$

the values for methyl alcohol, $\mathrm{E.P.}_{\mathrm{Ag}} = 0{\cdot}764$ and $\mathrm{L}_{\mathrm{AgBr}} = 5{\cdot}8 \,.\, 10^{-16}$,

$$\mathrm{E.P.}_{\mathrm{Br}} = +\,0{\cdot}849 \text{ volt.}$$

Standard Electrode Potential of Iodine.

The electromotive force of the cell,

$$\mathrm{Ag} - \mathrm{AgI} - \mathrm{I}_2,$$

is expressed by

$$-\mathrm{E} = \mathrm{E.P.}_{\mathrm{Ag}} - \mathrm{E.P.}_{\mathrm{I}} + 0{\cdot}05915 \log \mathrm{L}_{\mathrm{AgI}}.$$

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* *Loc. cit.*

Substituting the values for water, $\mathrm{E.P.}_{Ag} = 0{\cdot}7995$, $\mathrm{E.P.}_{I} = 0{\cdot}5357$, and $L_{AgI} = 1{\cdot}0 \,.\, 10^{-16}$,

$$E = +0{\cdot}6802 \text{ volt,}$$

which agrees fairly well with the directly-measured value 0·685 of Jones and Hartman *.

Substituting in the equation

$$-0{\cdot}683 = \mathrm{E.P.}_{Ag} - \mathrm{E.P.}_{I} + 0{\cdot}05915 \log L_{AgI}$$

the values for methyl alcohol, $\mathrm{E.P.}_{Ag} = 0{\cdot}764$ and $L_{AgI} = 6{\cdot}0 \,.\, 10^{-19}$,

$$\mathrm{E.P.}_{I} = +0{\cdot}369 \text{ volt.}$$

DISCUSSION OF RESULTS.

TABLE IV.

Element.	E.P. in water.	E.P. in methyl alcohol.	$\mathrm{E.P.}_{H_2O} - \mathrm{E.P.}_{MeOH}$.
Na	−2·7125	−2·728	+0·015
Tl	−0·3363	−0·379	+0·043
Cd	−0·398	−0·258	−0·140
H	0	0	0
Cu	+0·345	+0·490	−0·145
Ag	+0·7995	+0·764	+0·036
I......	+0·5357	+0·369	+0·167
Br	+1·0659	+0·849	+0·217
Cl	+1·3594	+1·128	+0·231

Table IV. gives the values which we have found for the standard electrode potentials of eight elements in methyl alcohol, together with the corresponding values in water. It will be seen that the relative positions of all the univalent elements are the same in both solvents, and that there is fairly close agreement between the two sets of values. All the univalent metals are rather more electropositive in methyl alcohol than in water by comparison with hydrogen, while the two divalent metals are considerably less electropositive. It must be remembered, however, that the activity coefficients are known with less certainty for the latter elements, as they have been calculated from the Debye-Hückel theory, whilst in the case of the univalent metals there is experimental support for taking them as equal to those of hydrogen chloride, which have been determined

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* J. Amer. Chem. Soc. xxxvii. p. 756 (1915).

directly. The differences between the values of the electrode potentials in the two solvents are greatest for the halogens.

If the process of ionization were solely the separation of a charged atom from the electrode, as postulated in the original Nernst theory, it might be expected that the electrode potentials should be independent of the solvent. However, there is little doubt that the passage of an ion from the crystal lattice into solution is accompanied by its association with a certain number of solvent molecules. Hence the electrode potential of an element represents the difference in the free-energy content of the ions in the lattice and in a solvated condition. It is, therefore, not surprising that there should be individual differences between the electrode potentials in the two solvents corresponding to the varying affinities of the molecules of the two solvents for the same ion. But, as hydrogen has been chosen as the standard of reference in each solvent, without any knowledge of the energy of solvation of hydrogen ions in both, it is difficult to draw any conclusions as to the relative affinities of the two solvents for individual ions. It is possible, however, to calculate from the electrode potential data the free energy of transfer of one mol of various electrolytes from a solution in water to a solution of the same activity in methyl alcohol.

Thus the combination

$$\mathrm{Cl_2}-\mathrm{HCl\ in\ methyl\ alcohol}-\mathrm{H_2}---\mathrm{H_2}-\mathrm{HCl\ in\ water}-\mathrm{Cl_2}$$

$$\xrightarrow[\quad E_3\quad]{\quad a_3\quad}\ \xleftarrow[\quad E_4\quad]{\quad a_4\quad}$$

$$\xleftarrow{\qquad E_5\qquad}$$

has an electromotive force,

$$E_5=E_4-E_3$$

and $$E_3=\mathrm{E.P.}_{\cdot\mathrm{Cl}}^{\mathrm{alc.}}-\mathrm{E.P.}_{\cdot\mathrm{H}}^{\mathrm{alc.}}-0\cdot1183\log a_3$$

and $$E_4=\mathrm{E.P.}_{\cdot\mathrm{Cl}}^{\mathrm{H_2O}}-\mathrm{E.P.}_{\cdot\mathrm{H}}^{\mathrm{H_2O}}-0\cdot1183\log a_4.$$

Since $\mathrm{E.P.}_{\cdot\mathrm{H}}^{\mathrm{alc.}}$ and $\mathrm{E.P.}_{\cdot\mathrm{H}}^{\mathrm{H_2O}}$ are taken as zero,

$$E_5=E_4-E_3=\mathrm{E.P.}_{\mathrm{Cl}}^{\mathrm{H_2O}}-\mathrm{E.P.}_{\cdot\mathrm{Cl}}^{\mathrm{alc.}}-0\cdot1183\log a_4/a_3,$$

and when the solute has the same activity in both solvents,

$$E_5{}^0=\mathrm{E.P.}_{\cdot\mathrm{Cl}}^{\mathrm{H_2O}}-\mathrm{E.P.}_{\cdot\mathrm{Cl}}^{\mathrm{alc.}}$$

From the figures given in Table IV., the free energy of transfer of one mol of hydrogen chloride from its solution of unit activity in water to that of unit activity in methyl alcohol is 5330 calories. Similar considerations for hydrogen bromide and hydrogen iodide lead to the values 5000 and 3850 calories respectively. These figures are inaccessible directly owing to rapid esterification making it impossible to measure the electromotive force of cells containing methyl alcohol solutions of these acids.

In addition, it is possible to calculate the free energy of transfer of thiocyanic acid from an aqueous to an alcoholic solution by making use of the data in Table III. to calculate the difference of standard potential between imaginary thiocyanogen electrodes in the two solvents.

Thus the combination

$$Ag-AgCNS-(CNS)_2$$

would have an electromotive force

$$-E = E.P._{Ag}^{H_2O} - E.P._{(CNS)_2}^{H_2O} + 0{\cdot}05915 \log L_{AgCNS}^{H_2O}$$

when water is the solvent, and the same when methyl alcohol is the solvent, viz.,

$$-E = E.P._{Ag}^{alc.} - E.P._{(CNS)_2}^{alc.} + 0{\cdot}05915 \log L_{AgCNS}^{alc.}.$$

Hence

$$\begin{aligned} E.P._{(CNS)_2}^{H_2O} - E.P._{(CNS)_2}^{alc.} &= E.P._{Ag}^{H_2O} - E.P._{Ag}^{alc.} + 0{\cdot}05915 \log L_{AgCNS}^{H_2O}/L_{AgCNS}^{alc.} \\ &= 0{\cdot}036 + 0{\cdot}05915 \log 84 \\ &= 0{\cdot}150 \text{ volt.} \end{aligned}$$

The free energy of transfer of one mol of thiocyanic acid from an aqueous to an alcoholic solution, both of unit activity, is thus 3460 calories.

The Quinhydrone Electrode.

The quinhydrone electrode has been studied in aqueous solutions by Biilman *, who obtained for the difference of potential between it and the hydrogen electrode the value 0·6990 volt. Using different preparations of quinhydrone and a variety of electrodes we have obtained for this potential difference the following results :—

Concentration of hydrogen chloride solution.	Concentration of quinhydrone.	E.M.F.
0·11 N.	0·006 m.	0·6989 volt.
0·01 N.	0·01 m.	$0{\cdot}6989_5$ volt.
0·01 N.	0·001 m.	0·6989 volt.
0·11 N.	0·005 m.	$0{\cdot}6990_7$ volt.

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* *Annales de Chimie*, xv. p. 109 (1921), and xvi. p. 320 (1921).

The quinhydrone electrode has been used in methyl alcohol by Ebert *, who measured the hydrogen and quinhydrone electrodes successively in portions of the same solution against an aqueous calomel reference standard. For the difference between them he got concordant values of 0·724 volt at 18° C.

We have made many attempts to measure the potential of the quinhydrone electrode in methyl alcohol, but have not succeeded in obtaining a steady value. In general the potential was found to rise steadily for from one to six hours, at the rate of from one to three centivolts per hour, and then to fall steadily at the rate of one to two millivolts per hour. In six experiments extrapolation of the observed electromotive force back to zero time led to values for the potential difference between the quinhydrone and hydrogen electrodes of 0·716, 0·715, 0·710, 0·718, 0·719, and 0·716 volt. Considerable momentary rises of electromotive force were produced when the solution was stirred by moving the platinum electrode, which suggests that the cause of these irregularities was some reaction by which the quinhydrone was destroyed at the electrode surface. Addition of further quantities of quinhydrone to the solution produced a considerable rise of potential, which was not, however, reproducible. Removal of the platinum electrode, and heating it to redness in an alcohol flame produced a rise of potential of several centivolts, but the subsequent fall was rapid. In attempts to find the cause of these disturbances we have used different specimens of quinhydrone and electrodes of gold, of platinum gauze, and of bright platinum foil. Solutions of hydrogen chloride, of benzenesulphonic acid, and buffer solutions of succinic acid and guanidine succinate have given equally unsatisfactory results.

The Dissociation Constant of Methyl Alcohol.

The hydrogen electrode was used to measure the hydrion concentration in a solution of sodium methylate, and hence to calculate the dissociation constant of methyl alcohol.

Sodium methylate solution free from water and carbon dioxide was made by a method due to Mr. W. F. K. Wynne-Jones. Pieces of sodium as free as possible from oxide were melted under paraffin in a Pyrex flask, and drawn up into thin-walled glass tubing about 2 mm. in diameter. This was cut into convenient lengths, and the central portions dropped quickly into a flask containing methyl alcohol.

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* *Berichte,* lviii. p. 175 (1925).

When the reaction was completed, the concentration of the solution was found by weight titration against standard acid.

The hydrogen was generated electrolytically from sodium hydroxide solution saturated with baryta, using nickel electrodes. It was freed from traces of oxygen by passing over a heated tungsten filament, dried with sulphuric acid, soda lime, and phosphorus pentoxide, and then saturated with alcohol vapour before entering the cell. It was found impossible to get a steady potential when using freshly iridized gold plates as hydrogen electrodes, and after several failures with platinum electrodes satisfactory results were obtained with one that had been freshly platinized.

The combination

$$\begin{array}{ccc|cc} & \text{MeONa} & & \text{NaCl} & \\ H_2 & & & & \text{AgCl, Ag} \\ & 0{\cdot}0217\text{ m.} & & 0{\cdot}01\text{ m.} & \\ & & + & - & \end{array}$$

$$1{\cdot}7\text{ mv.}$$

gave an electromotive force of 0·9930 volt. A correction of 1·7 mv. is to be added for the potential at the liquid junction and of 2·3 mv. to correct the hydrogen electrode to a partial pressure of hydrogen gas of one atmosphere. The secondary reference electrode had a potential of 0·047 volt referred to Ag, AgCl 0·1 m. NaCl, so that the potential of the hydrogen electrode in the sodium methylate solution referred to the standard hydrogen electrode was $-0{\cdot}879$ volt.

Hence

$$\log a_{\mathrm{H}} = -\frac{0{\cdot}879}{0{\cdot}05915} = \overline{15}{\cdot}1395.$$

If the activity coefficient of 0·0217 m. sodium methylate solution is 0·652, the dissociation constant of methyl alcohol is calculated to be $1{\cdot}95 \,.\, 10^{-17}$.

In a second experiment using a 0·0626 molal sodium methylate solution, the observed electromotive force was 1·0684 volt with a calomel reference electrode whose potential was $-0{\cdot}170$ volt relative to the standard hydrogen electrode. Adding 2·3 mv. for the barometric correction, and 2·8 mv. for the liquid junction potential, the potential of the hydrogen electrode in the sodium methylate solution was $-0{\cdot}9035$ volt referred to the standard hydrogen electrode. Hence

$$\log a_{\mathrm{H}} = -\frac{0{\cdot}9035}{0{\cdot}05915} = \overline{16}{\cdot}73.$$

If the activity coefficient of 0·0626 molal sodium methylate solution is 0·515, the dissociation constant of methyl alcohol is calculated to be $1\cdot73 \,.\, 10^{-17}$. Less reliance is placed on this value than the first, as the electromotive force of the cell fell off after half an hour.

Previous determinations of this constant have yielded the following results:—

(i.) Carrara, by measurements of electromotive force at 10° C., got $4\cdot9 \,.\, 10^{-17}$.

(ii.) Bjerrum, Unmack, and Zechmeister *, by a somewhat doubtful extrapolation to infinite dilution from two points, obtained $3\cdot6 \,.\, 10^{-17}$.

(iii.) Wynne-Jones, in experiments (not yet published) on the alcoholysis of salts in methyl alcohol, found values varying from $3\cdot0$ to $2\cdot0 \times 10^{-17}$.

SUMMARY.

(1) A study has been made of reference electrodes, of liquid-junction potentials, and of activity coefficients in methyl alcohol.

(2) Measurements have been made of the standard electrode potentials of nine elements, and the results used for determining the solubilities of five sparingly soluble salts and the dissociation constant of methyl alcohol.

(3) The quinhydrone electrode has been studied in aqueous and alcoholic solutions.

Physical Chemical Laboratory,
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February 1929.

XXXIX. *Unbalance in Circuits.* *By* M. REED, *M.Sc.* (*Lond.*), *A.C.G.I.*, *D.I.C.* (*Research Laboratories, International Standard Electric Corporation*) †.

1. *General.*

IN cases where accurate measurements have to be made, it is found that, in addition to the normal impedances, it is necessary to take into consideration the admittance to ground of various parts of the circuits under investigation. These admittances are generally very small, yet under certain conditions their effect on the measurement can be quite appreciable. This paper considers how these admittances can influence the accuracy of a given measurement, and also how it is possible to avoid the errors that would result from their presence.

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* *Kgl. Danske Vid. Selsk. Mat.-fys. Medd.* V. ii (1924).

† Communicated by the Author.

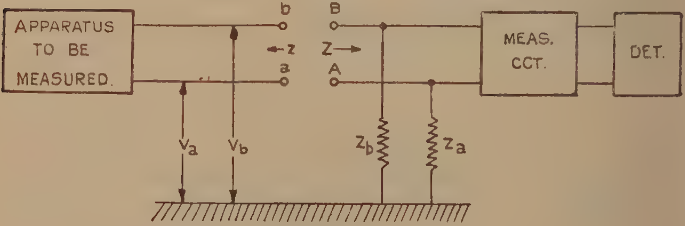
2. *Longitudinal Voltages.*

Suppose that it is required to measure the voltage between the terminals of a given piece of apparatus. Assume that this voltage is to be measured by means of a circuit which possesses a pair of input terminals, and which comprises a detector of some sort to indicate the value of the voltage which may be impressed across these input terminals.

It will be shown that it is necessary, in determining the behaviour of the circuit, to consider not only the impedance between the input terminals, but also the admittance to ground of each terminal. In the general case, when these admittances are unequal, it will be found that the voltage produced across the terminals of the apparatus under consideration will be measured incorrectly if the average voltage from these terminals to ground is not zero.

Consider the circuit of fig. 1.

Fig. 1.



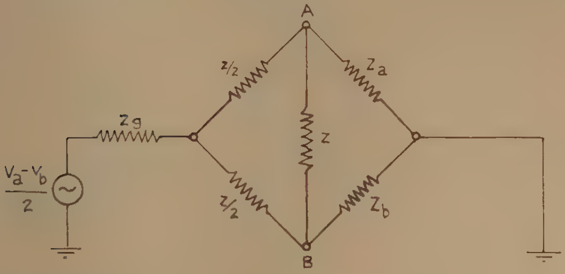
In this diagram assume that :—

z =impedance measured between terminals a and b.
V_a=magnitude of voltage between terminal a and ground.
V_b= ,, ,, ,, ,, ,, b ,, ,,
Z =impedance measured between terminals A and B.
Z_a= ,, ,, ,, terminal A and ground.
Z_b= ,, ,, ,, ,, B ,, ,,

If we assume that the physical mid-point of z is connected either directly or through an impedance Z_g to ground, then if V_a is not equal to V_b, the physical mid-point of z will not coincide with the electrical zero. The difference between V_a and V_b may be due to a number of causes, *e.g.*, unbalance in coils and transformers, interference from outside sources. The potential of the mid-point will therefore differ from that of ground by an amount given by $\frac{V_a \sim V_b}{2}$. Under these circumstances the circuit of fig. 1 can be regarded as equivalent to that of fig. 2.

In some cases the value of the impedance, as measured between the mid-point and terminals A and B, will not be equal to $\frac{z}{2}$, but to some value which is less than half of the value of the impedance as measured between A and B. The value of the impedance between each terminal and the mid-point will, however, be the same; hence the diagram of fig. 2 will still be true in principle.

Fig. 2.

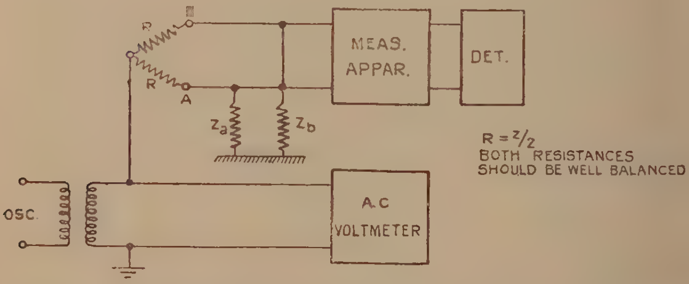


The voltages V_a and V_b are not shown, as they only give the voltage which would normally be measured across A and B.

Fig. 2 shows that the unbalance voltage $\frac{V_a \sim V_b}{2}$ acts across a circuit which is equivalent to a Wheatstone Bridge. It therefore follows that if Z_a is not equal to Z_b, then there will be a difference of potential set up across AB whose value will depend on the values of $\frac{1}{2}(V_a \sim V_b)$ and Z_g. The measuring circuit will record this voltage, in addition to the normal voltage, and hence there will be an error introduced into the measurement. The unbalance current, and therefore the error, will be increased as the value of Z_g is reduced, the error being a maximum when $Z_g=0$. It is therefore undesirable that the mid-point of z should be connected directly to earth. If $Z_a=Z_b$, then there will be no unbalance current through Z, and the correct voltage will be measured. It is therefore necessary, in order that accurate and consistent results should be obtained, that the value of Z_a should be made equal to that of Z_b.

The above phenomenon, which is caused by the unbalance voltage $\frac{1}{2}(V_a \sim V_b)$, is said to be produced by a longitudinal voltage. This is to distinguish it from any voltage which acts across the terminals AB, and which is called a transverse voltage. A measure of the error introduced by the longitudinal voltage can be obtained in the following manner.

Fig. 3.



The circuit of fig. 3 is fitted up and the voltage V_1 produced by the oscillator is adjusted until some convenient reading is obtained on the detector. The value of this voltage is obtained from the a.c. voltmeter, which may consist of a suitable thermocouple with a series resistance. The voltage V_2 necessary to produce the same reading on the detector when the oscillator is applied to the terminals AB is then measured, care being taken that the oscillator used is well balanced to ground. The ratio V_2/V_1 will then give the value of the transverse voltage, which is equivalent to 1 volt of longitudinal voltage, and hence it will be a measure of the error that would be introduced into a given measurement.

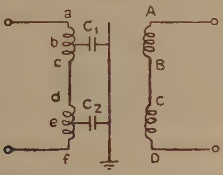
When making this test care should be taken that the leads (if any) between the resistances R and the terminals AB do not introduce ground unbalances. If leads are used they should be short and unscreened. They can be tested for ground unbalances by reversing the connexions at A and B on the set. The value of V_1 should be unaltered by the reversal.

3. *The Balanced and Screened Transformer.*

It will be shown later that in the case of certain circuits it is desirable, in order to avoid the errors due to longitudinal voltages, to employ balanced and screened transformers. A brief description of this type of transformer is given below.

Each winding of the transformer consists of two sections, each section being wound to cover one-half of the core. The turns on the two sections, which comprise one winding, are adjusted until the sections are balanced. A shield is placed between the two windings, and the side of the transformer which is to be balanced is so wound that the capacities between the shield and each half of the winding are equal and symmetrically located with respect to the mid-point of the whole winding. This is accomplished by winding the sections *ab* and *de* and the sections *bc* and *ef*, each as twisted pairs. The total capacity of each section of the same winding will then be practically the same. Consider, for example, the transformer of fig. 4.

Fig. 4.

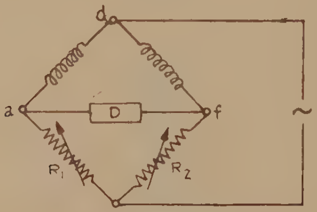


The windings *af* and AD would each consist of two sections. The sections *ac* and *df* of winding *af* would be balanced. Similarly the sections AB and CD of winding AD would be balanced. If it is required that the winding *af* should be balanced with respect to the shield, then this winding would be so arranged that the capacities C_1 and C_2 should act at points which are equidistant from the mid-point *cd*. It would then be found that C_1 did not differ appreciably from C_2. A similar procedure would be adopted if it were desired to balance the winding AD to shield.

Further, owing to the presence of the shield, which is always earthed, there is no direct capacity between the windings *af* and AD. Hence any unbalance to earth which may occur on the right-hand side of the transformer will be completely cut off from the left-hand side.

The degree of unbalance between two sections of a winding can be very easily determined by the following method. The two sections are connected up with two resistance boxes to form a bridge of the form shown in fig. 5. The resistance boxes are then adjusted until the bridge is balanced, and the ratio of the values of the resistances gives a measure of the unbalance between the sections. The two sections can then be adjusted until the resistance ratio is unity, thus indicating zero unbalance.

Fig. 5.



4. *Unbalances in Practice.*

In practice unbalances are important because, as seen from fig. 2, they enable the longitudinal voltage to give rise to currents which are circulating, and which are therefore not attenuated by any apparatus that may be present in the circuit. In cases where this apparatus has high attenuation, the current due to the normal transverse voltage is greatly attenuated, whereas the currents due to the longitudinal voltage remain unattenuated. It is therefore quite possible, when the attentuation is very high, that the voltage produced at the far end by the circulating currents may be comparable with that produced by the normal current. The error introduced in this case would be fairly large.

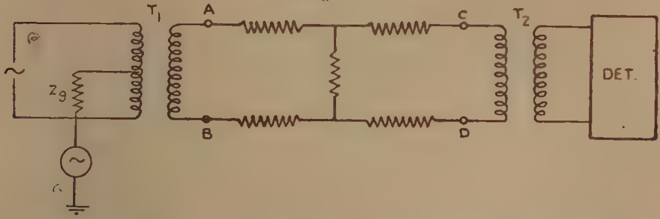
It follows that if the unbalances in the circuit are such that they produce a transverse and not a longitudinal unbalance voltage, then the current which is derived from this voltage will suffer the same attenuation as the legitimate current, and hence the error introduced in a given measurement will be negligible.

In practice, measuring circuits are either of the balanced or of the unbalanced type. Each type will now be considered in detail, and it will be shown, in each case, how the accuracy of measurement is affected by unbalances in the circuit, and also how the errors can be avoided.

5. *The Balanced Circuit.*

In this type of measuring circuit the admittance to ground of all the terminals is assumed to be the same. Also the value of the impedance of each series arm is the same.

Fig. 6.



Consider, for example, the circuit of fig. 6, in which it is assumed that the balanced circuit is represented by the networks ABCD. This network is connected to an oscillator and a detector through transformers T_1 and T_2, respectively.

Assume that the terminals of the oscillator have different voltages to ground, so that we have in effect a potential difference between the mid-point of the primary winding of T_1 and ground. It is assumed that this mid-point has an impedance Z_g to ground. The following cases must now be considered.

5 (1). T_1 *and* T_2 *both without shields.*

If T_1 is without a shield, then the unbalance voltage will be transferred from the primary to the secondary side of T_1 through the stray capacity that will exist between the windings. Further, since T_2 has no shield, it is very probable that the admittance to earth of terminal A will be different from that of terminal B. Hence we shall find, on replacing the circuit of fig. 6 by one similar to that of fig. 2, that there will be an unbalance current produced in winding CD. This current will give rise to a voltage across CD which will be transferred to the terminals of the detector, thus causing an error in the measurement. It will be noticed that the unbalance current is not attenuated by the network ABCD, and therefore it is quite possible, when the attenuation is high,

Fig. 7.

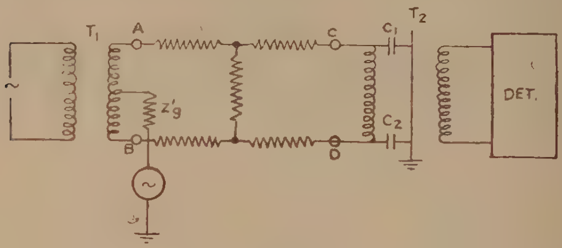
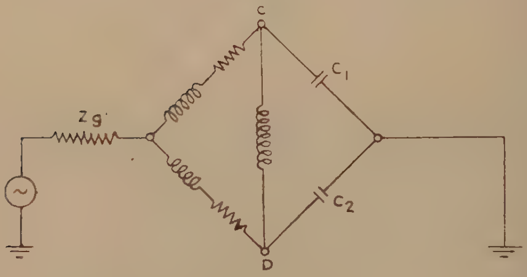


Fig. 8.



that the voltage across CD which is derived from the unbalance current may be comparable with that derived from the normal current.

5 (2). T_2 *has a shield, and winding* CD *is balanced to shield.*

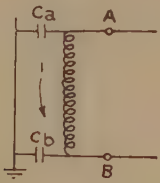
Assuming that T_1 is still without a shield, then the conditions are as indicated in fig. 7.

This circuit can be reduced to that of fig. 8. It can be seen from this diagram that the longitudinal voltage will produce no current in the winding CD, provided that $C_1 = C_2$.

5(3). T_1 *and* T_2 *both shielded, and windings* AB *and* CD *balanced to their respective shields.*

T_1 now has an earthed shield, therefore it is impossible for the longitudinal voltage to be transferred from the primary to the secondary side of T_1. It is possible, however, for a longitudinal voltage to be obtained on the secondary side of T_1 under the following conditions. Consider fig. 9, and assume that the secondary of T_1 is not perfectly balanced to shield, that is, capacities C_a and C_b are not equal.

Fig. 9.



The voltage across AB will set up a current I, as shown in fig. 9. If C_a is not equal to C_b, then the voltage drop across these condensers will be different, and therefore the potential of the point A with respect to the shield (*i.e.*, to ground) will not be the same as that of point B. This condition is identical with that of fig. 1, and hence there will be a potential difference between the mid-point of the winding AB and earth. The problem will therefore reduce to that of case 5(2), and we shall obtain unbalance current in winding CD unless $C_1 = C_2$.

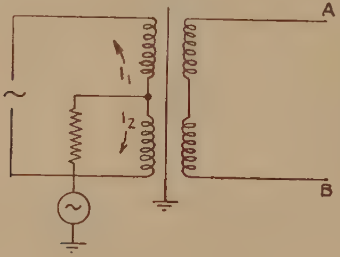
5 (4). *Unbalance between the two sections of the primary* T_1.

There is one further unbalance to be considered. Suppose that there is a slight unbalance between the two sections of the primary of T_1, and suppose further that we still have an unbalanced voltage to ground. The conditions will then be as indicated in fig. 10.

The currents I_1 and I_2 will be unequal, and the resultant current will set up an e.m.f. across the primary of T_1. This voltage will be transferred to the secondary side, but, since it appears as a transverse voltage, the current resulting from it will be attenuated by the network ABCD. The final voltage across winding CD will therefore be extremely small, and the error introduced will be negligible. It is necessary, however, to maintain a fairly close balance between the sections, otherwise it will not be possible to obtain a high degree of balance between the primary winding and the shield in those cases where it is necessary to balance the primary side of T_1.

From 5(1), 5(2), and 5(3) we can deduce that, when dealing with a balanced measuring circuit, it is essential, in order to obtain accurate and consistent results, that both T_1 and T_2 should have shields. In addition, the secondary winding of T_1 and the primary winding of T_2 must be very closely balanced to their respective shields. If these precautions are not taken, then it is possible for conditions 5(1), 5(2), and 5(3) to occur either singly or together.

Fig. 10.



6. *The Unbalanced Circuit.*

In this type of circuit there is no assumption made with reference to the admittance to ground of the terminals. Also all the series impedances are contained in one side of the circuit.

In fig. 11 the network PQRS is meant to represent an unbalanced circuit. It is assumed that this network is connected to the oscillator and detector, respectively, by means of the transformers T_3 and T_4. Assume further that there is an unbalance voltage to ground on the primary side of T_3, and consider the following cases.

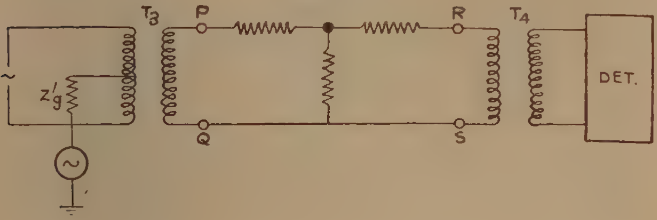
6 (1). T_3 *and* T_4 *have no shields.*

This case is identical with that of 5 (1), and we shall, in all probability, have an unbalance current in winding RS.

6 (2). T_4 *has a shield, and winding* RS *is balanced to shield.*

In this case, even though the balance of winding RS to shield may be perfect, yet there will probably be an unbalance current in this winding. If we reduce fig. 11 to a Wheatstone Bridge similar to that shown in fig. 8, it will be seen that one of the arms will contain the whole of the series impedance of the network; hence the bridge will be unbalanced, and we shall obtain an unbalance current in winding RS.

Fig. 11.



6(3). T_3 *and* T_4 *both have shields and windings* PQ *and* RS *are balanced to their respective shields.*

If T_3 has a shield, then the longitudinal voltage cannot be transferred from the primary to the secondary side of T_3. Since the terminals P and Q are not balanced to ground, it is extremely probable that the voltage to ground of terminal P will be different from that of terminal Q; hence the mid-point of winding PQ will have some potential to ground. This case will therefore reduce to the one dealt with under 6 (2).

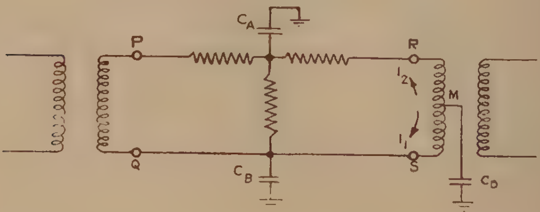
Cases 6 (2) and 6 (3) indicate that, even if T_3 and T_4 both have shields and the appropriate windings balanced to these shields, it is still possible to obtain an unbalance current in winding RS.

6 (4). *Capacity to earth of the network.*

In addition to the unbalances already considered, we have to consider the capacity to earth of the various members of the circuit. Assuming that there is no longitudinal voltage present, the circuit of fig. 11 can be replaced by that of fig. 12, where C_A, C_B, and C_D are capacities to earth of different components of the circuit. It is assumed that these capacities can be located at the mid-points of the respective elements.

From fig. 12 it is seen that the voltage across PQ acting in series with C_A and D_D will produce a current I_1 in MS. Similarly this voltage, acting in series with C_B and C_D, will produce a current I_2 in MR. In general these two currents will be unequal, and the resultant current will set up a voltage across RS which will be transferred to the terminals of the detector and will cause an error in the measurement. It will be seen that the value of this unbalance current will not be influenced by the value of the attenuation in the network PQRS.

Fig. 12.



This source of error does not arise in the case of the balanced network, because it is assumed that in this type of circuit $C_A = C_B$; hence the currents I_1 and I_2 will be equal.

6 (5). *One side of the network connected to earth.*

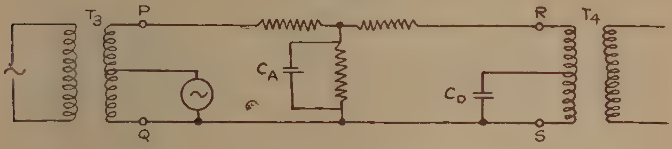
Suppose now that one side of the network PQRS is connected to earth. In this case C_B will be short circuited, C_A and C_B will be connected as shown in fig. 13, and any longitudinal voltage that may exist on the secondary side of T_3 will act across one-half of the winding PQ.

This voltage can therefore be replaced by a voltage acting across PQ, that is, a transverse voltage, and hence any current that it produces will be attenuated by PQRS. In addition, it is seen from fig. 13 that it is now impossible for the capacities C_B and C_D to produce a circulating current as in case 6 (4).

Hence by the above arrangement it is possible to avoid errors that would arise owing to unbalances in the circuits or the capacities to earth of various members of the circuits. If the side is not earthed as in fig. 13, then it is possible for all or any number of the conditions 6 (1), 6 (2), 6 (3), and 6 (4) to occur at the same time.

It will be seen from fig. 13 that it is unnecessary to balance to shield either the secondary side of T_3 or the primary side of T_4. It will only be necessary to shield T_3 and to balance the primary winding to shield if the oscillator output is balanced. The same applies to the secondary winding of T_4 if the detector input is balanced.

Fig. 13.



In the foregoing it has been assumed that the frequency is not sufficiently high for the capacities C_B and C_D to offer paths of low impedance to the normal current.

7. *Conclusions.*

The above analysis indicates that, where possible, it is desirable to use an unbalanced measuring circuit with one side earthed. With this type of circuit it is possible to eliminate most of the errors that arise from unbalances. Where it is essential to use a balanced measuring circuit, it is necessary to employ shielded and well-balanced transformers in order to obtain consistent and accurate results.

When connecting a balanced to an unbalanced circuit, the circuits must be separated by a shielded transformer which is balanced on the side which is connected to the balanced circuit.

XL. *The Magnetic Susceptibility of Cæsium in the Solid and Liquid State.* By C. T. LANE, *M.Sc., National Research Student, Canada* *.

[Plate VIII.]

1. *Introduction.*

PAULI, in his notable contribution of 1927 †, was the first to give a satisfactory theory for the phenomenon of paramagnetism in metals. Very briefly he has considered the free electrons in a metal to constitute an ideal "gas" degenerate at all ordinary temperatures. Making use of the Fermi distribution function for such a gas, he has arrived at the result that the alkali metals should all be paramagnetic. Further, he has shown that the variation of susceptibility with temperature in these elements should be negligible. The theory, however, neglects the possible diamagnetic contribution to the susceptibility of the atom cores. Thus we are led to predict a paramagnetic value of the susceptibility in the case of copper, silver, and gold, whereas there seems little doubt but that these metals are diamagnetic.

If we calculate the diamagnetic contribution of the atom cores on purely classical principles, we are led to the conclusion that K, Rb, and Cs are actually diamagnetic ‡. In a recent article, however, Rosenfeld § has estimated the diamagnetic effect by making use of a calculation due to Bethe of the "lattice potential" in metals. He shows the diamagnetic contribution to be a function of the "lattice potential" (V_0) related by the expression

$$\chi_d = -\frac{eV_0}{4\pi mc^2},$$

where e, m, and c have their usual significance. The quantity V_0 of course can be determined from electron beam diffraction experiments, and applying this correction to the Pauli result, Rosenfeld arrives at a diamagnetic susceptibility for Cu, Ag, and Au. The correction has not been applied to the alkali metals owing to lack of information regarding V_0 for these elements.

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* Communicated by Dr. A. S. Eve, F.R.S.

† W. Pauli, *Zeits. f. Physik*, xli. p. 81, Feb. 1927.

‡ *Cf.* E. S. Bieler, Journ. Frank. Inst. ccvi. p. 77 (July 1928).

§ L. Rosenfeld, *Naturwissenschaften*, xvii. p. 49 (Jan. 1929).

In the case of the alkali metals K, Na, and Rb, a number of independent experimental investigations have been made which are in good agreement with one another, and also in fairly good agreement with the values predicted by Pauli. In the case of cæsium, however, upon which, up to the present work, four investigations * have been made, the results are extremely divergent. Three observers find a diamagnetic value for the metal, whilst the fourth finds it paramagnetic. Again, two investigations on both the solid and liquid state have been made (by Owen and Sucksmith respectively). One observer finds no change in the susceptibility at the melting-point, while the other finds such a change.

In view of the theoretical interest involved in this subject, the author has reinvestigated cæsium in both the solid and the liquid state in the hope of definitely settling the value of the susceptibility. The results of this investigation are communicated in the following pages.

2. *Preparation of the Metal.*

The cæsium metal was obtained from Messrs. Einer and Amend, New York, and was guaranteed as "chemically pure." Nevertheless it was decided, in view of the importance of avoiding ferromagnetic impurity, to subject the metal to multiple distillation. The samples as obtained from the makers were in ½ gram lots, packed in oil. The problem of obtaining a suitable specimen, therefore, resolved itself into first separating the metal from the oil and, secondly, distilling it. The method finally adopted, after considerable preliminary trial, was that of fractional distillation of the metal from the oil, which has a considerably lower boiling-point than the cæsium. It was necessary, of course, that the whole operation should take place in a high vacuum.

Fig. 1 is a diagrammatic sketch showing the form of distilling apparatus finally adopted. A Langmuir mercury pump fitted with a liquid air-trap L, and backed by a "Hy-vac" pump, was the means of producing the required vacuum. The distilling apparatus proper consisted of a bulb B with a charging-tube F fitted with a ground-glass stopper W. The specimen tube into which the metal was distilled is shown at S. The distilling apparatus connected into the vacuum system through an oil-trap O and a small discharge-tube T.

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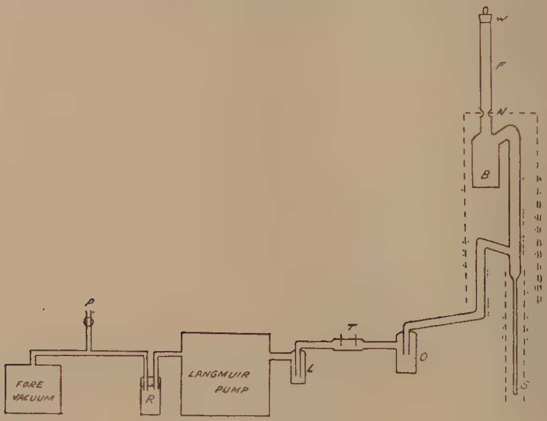
* These investigations are contained in the following papers:—M. Owen, *Ann. der Physik*, xxxvii. p. 657 (1912). L. Crow, Proc. Roy. Soc. Canada, III. xix. p. 63 (1925). W. Sucksmith, Phil. Mag. ii. p. 21 (1926). McLennan, Ruedy, and Cohen, Proc. Roy. Soc. A, p. 468 (Oct. 1927).

The apparatus is first pumped down and filled with nitrogen-gas through P. The metal and oil at about 30° C. are then introduced into B with a pipette. The apparatus is then re-evacuated and the charging-tube sealed off at the neck N. An electric furnace is now placed over the apparatus as indicated by the dotted lines, and a special heater (also shown dotted) is placed over the specimen-tube. These furnaces are both adjusted to about 200° C. and the oil distilled into the trap O. When all the oil has been distilled over a smaller electric furnace is placed over B, adjusted to 400° C., and the metal distilled into S.

Fig. 1.



Distillation Apparatus.

In the present experiment this operation was done, in all, three times. In the first two cases all the metal and some protecting oil were distilled into S. In the final operation all the oil was removed and about three-quarters of the total metal in B was distilled over into S. A specimen of triply distilled cæsium completely free from oil was thus obtained.

Jena glass was employed in the construction of the apparatus as being the most suitable for the work in hand. The specimen-tube was of the same material, roughly 18 cm. long and 0·35 cm. in diameter.

3. *Method of Measurement.*

A modified form of the Gouy * method for measuring the susceptibility was employed wherein the specimen in the form of a long cylinder is suspended between the poles of an electromagnet, the cylinder having its axis perpendicular to the lines of force. The downward force on the cylinder is given by the relation

$$P=\tfrac{1}{2}\times Ad(H_1^2-H_0^2),$$

where P = force in dynes,

x = mass susceptibility,

A = cross sectional area of cylinder in cm.^{2},

d = density of cæsium,

H_1 = field in gauss in the magnet gap,

H_0 = field in gauss at the other extremity of the cylinder.

The force P was measured by means of a sensitive balance accurate to better than 1/50 mg. The magnetic field was produced by a large Weiss electromagnet with water-cooling arrangements. An aluminium housing was built around the magnet for the purpose of shielding the specimen from draughts. A mica window was provided in the housing so that the specimen could be observed at all times. A thermometer could also be observed through this window.

A certain degree of temperature control could be maintained inside the specimen-chamber by varying the rate of flow of water through the magnet-cooling coils. The measurements in the solid state were taken at about 15° C., and those in the liquid state at about 28° C.

The measurements on the solid state were done by the method similar to that employed by Také Soné † and McLennan, Ruedy, and Cohen ‡, wherein the effect of the glass tubing is automatically compensated for. Experiments on the empty tube showed the latter to be compensated to within less than 0·5 per cent. For the liquid state, on the other hand, it was feared that vapour in the upper part of the specimen-tube might affect the result. The unmodified Gouy method was therefore employed and a blank test was made for the glass container at the same temperature. In both cases the susceptibility was determined by a number of different field strengths. The magnetic field was measured by means of a null method originally due to Ellis and Skinner*, but discovered independently by the writer†. The method consists essentially in reducing a known current in the primary of a mutual inductance to zero, while the search-coil is cutting the lines of force. The mutual inductor secondary, the search-coil, and a ballistic galvanometer are connected in series. The instrument used in the present experiment is shown in the accompanying photograph (Pl. VIII.). The search-coil is wound on a long rectangular glass frame S, consisting of two turns of wire. One extremity of the search-coil moves wholly within the uniform field of the gap, whilst the other moves in a region where the field is negligible. The search-coil is mounted on a brass carriage M and can move a fixed distance in the horizontal direction. The carriage M carries a contact C (insulated from it) which slides over a wire resistance W connected to heavy brass plugs at each end. The function of this resistance is to provide approximately the same waveform in the mutual inductance secondary as that produced by the search-coil in cutting the lines of force. The binding posts are connected as shown, those marked HH being connected to the search-coil. In operation a 2-volt storage-cell is connected permanently across BB. Leads from the B terminal and P go to a mutual inductance primary *via* a control resistance. The search-coil, the secondary of the mutual inductance, and a ballistic galvanometer are connected in series. The current in the mutual inductance primary is then adjusted until the galvanometer is balanced, whence

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* Stoner, 'Magnetism and Atomic Structure,' p. 40.

† Také Soné, Phil. Mag. xxxix. p. 305 (1920).

‡ *Loc. cit.* p. 472.

$$H=\frac{MI}{NA},$$

where H = magnetic field in the gap,
M = coefficient of mutual induction,
I = steady current in mutual inductance primary,
A = area swept out by search-coil conductors,
N = number of search-coil turns.

Balance could be obtained with this instrument to better than 1 part in 2000. In the present work the field measurements are accurate to probably 0·25 per cent., a major portion of this error being due to fluctuations in the magnet-exciting current. A survey of the field in the vicinity of the magnet showed that H_0^2 was entirely negligible as compared to H_1^2.

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* Ellis and Skinner, Proc. Roy. Soc. A, cv. p. 60 (1924).

† C. T. Lane, Journ. Sci. Inst. v. p. 214 (July 1928).

Results.

The results for the solid and liquid states are given in Tables I. and II. respectively. In each case the results are for the specific or mass susceptibility, the density of cæsium for the solid and liquid states (1·90 and 1·84 respectively) being taken from the International Critical Tables. In fig. **2** a curve is plotted showing the relation between susceptibility and magnetic field strength. As is seen, this curve does not depart from a straight line parallel to the field axis by more than approximately 1 per cent., which is within the experimental error. Further, Owen has shown[*] that if iron

TABLE I.

Solid state (15° C.).

Current in magnet coils. Amps.	Force (P). Milligrams.	Magnetic field. Gauss.	Specific susceptibility.
1·4	$0{\cdot}46_5$	4780	$+0{\cdot}21_8 \times 10^{-6}$
2·0	0·95	6810	$0{\cdot}22_0$
2·5	1·47	8440	$0{\cdot}21_7$
3·0	2·08	10100	$0{\cdot}21_9$
3·3	$2{\cdot}49_4$	11100	$0{\cdot}21_7$
3·6	3·01	12150	$0{\cdot}21_9$
4·0	$3{\cdot}74_7$	13520	$0{\cdot}21_9$
4·3	4·21	14400	$0{\cdot}21_8$
4·6	4·81	15370	$0{\cdot}21_8$
5·0	5·64	16620	$0{\cdot}22_0$
5·4	6·57	18000	$0{\cdot}22_8$
5·8	7·51	19100	$0{\cdot}22_0$
6·2	8·43	20300	$0{\cdot}22_0$
6·6	9·41	22200	$0{\cdot}22_1$
7·0	10·14	22200	$0{\cdot}22_0$
7·5	10·82	22900	$0{\cdot}22_1$
9·0	12·14	24200	$0{\cdot}22_3$

Mean value $+0{\cdot}22 \times 10^{-6}$.
Diam. spec. $0{\cdot}0963_3$ sq. cm.
Density 1·90.

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[*] M. Owen, *loc. cit.*

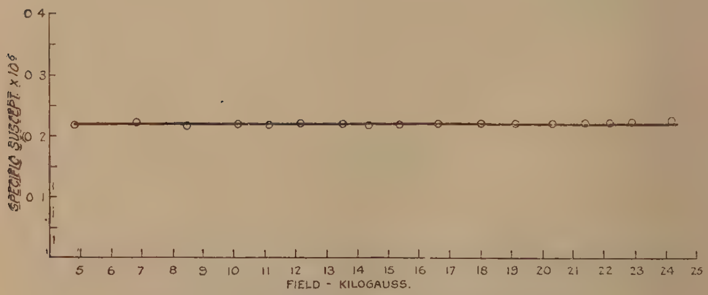
Table II.

Liquid state (28° C.).

Current in magnet coils. Amps.	Force (P). Milligrams.	Magnetic field. Gauss.	Specific susceptibility.
3·0	1·80	10100	$+0{\cdot}19_6 \times 10^{-6}$
3·3	2·20	11100	$0{\cdot}19_8$
3·6	2·61	12150	$0{\cdot}19_8$
4·0	3·27	13520	$0{\cdot}19_7$
4·6	4·24	15370	$0{\cdot}19_9$
5·0	4·90	16620	$0{\cdot}19_6$
5·4	5·83	18000	$0{\cdot}20_0$
5·8	6·50	19100	$0{\cdot}19_7$
6·2	7·34	20300	$0{\cdot}19_8$
6·6	8·25	21400	$0{\cdot}20_0$
7·0	8·84	22200	$0{\cdot}19_8$
7·5	9·32	22900	$0{\cdot}19_7$
8·0	9·75	23400	$0{\cdot}19_8$
9·0	10·44	24200	$0{\cdot}19_7$

Mean value $+0{\cdot}20 \times 10^{-6}$.
Diam. spec. $0{\cdot}0963_3$ cm.
Density 1·84.

Fig. 2.



Curve showing relation between Susceptibility and Field Strength.

impurity be present in the specimen, we should have the following relation between susceptibility and field strength, viz.:

$$x = x_0 + \frac{\sigma}{\mathrm{H}},$$

where x = measured susceptibility,

x_0 = "iron free" value of the susceptibility,

σ = saturation intensity of magnetization of the uncombined iron impurity,

H = magnetic field strength.

The susceptibility should therefore decrease with increasing field according to a hyperbolic law if any noticeable iron impurity be present.

In Table III. are collected together the four existing results on cæsium in the solid state, together with that found in the present experiment.

The agreement between the present results and that of McLennan, Ruedy, and Cohen appears to be quite good in the case of the solid state. As mentioned previously, the only results in the liquid state are those of Owen and Sucksmith.

TABLE III.

Cæsium (solid state).

Observer.	Owen. 18° C.	Crow. 20° C.	Sucksmith. 0° C.	McLennan, Ruedy, & Cohen. (None stated.)	Author. 15° C.
Specific suscept.	$-0{\cdot}10\times10^{-6}$	$-0{\cdot}06\times10^{-6}$	$-0{\cdot}05\times10^{-6}$	$+0{\cdot}18\times10^{-6}$ $+0{\cdot}22\times10^{-6}$	$+0{\cdot}22\times10^{-6}$

The present work is in disagreement with Owen, who found no change in susceptibility between liquid and solid state. On the other hand, Sucksmith found a decrease in the diamagnetic susceptibility at the melting-point, whereas the writer finds a decrease in paramagnetic susceptibility in passing over into the liquid state.

The agreement with the value predicted by Pauli is reasonably good, as is here shown:

Calculated (Pauli) $+0{\cdot}24\times10^{-6}$.

Observed (Author) $+0{\cdot}22\times10^{-6}$ (solid state).

The probable error of the measurement of susceptibility in the solid state is about 1·5 per cent., while that in the liquid state is probably somewhat higher.

The present state of our knowledge of the susceptibility of the alkali metals is given in Table IV., which quotes the most trustworthy values of the metals Na, K, and Rb. So far as the author is aware this table contains all the recent results on these metals.

TABLE IV.

Observer.	Owen.	Sucksmith.	McLennan, Ruedy, & Cohen.	Author *.	Pauli (calculated).
Sodium	$+0.51\times10^{-6}$	$+0.59\times10^{-6}$	$+0.59\times10^{-6}$	$+0.65\times10^{-6}$	$+0.67\times10^{-6}$
Potassium ...	0·40	0·51	0·45	0·54	0·60
Rubidium ...	0·07	0·07	0·17	—	0·32

It is a pleasure to record my thanks to Dr. A. S. Eve, Director of the Physics Department, for his encouragement and advice, and also to Dr. L. V. King for many helpful discussions. I am indebted, further, to the National Research Council of Canada for a studentship during the tenure of which this work was done. Finally, I add to Dr. E. S. Bieler, whose death we deplore, a tribute for his enthusiastic guidance of my career in physics, and of my work in magnetism.

Macdonald Physics Laboratory,
McGill University,
March 1929.

XLI. *Cathode Phenomena in Geissler Discharges through Oxygen and Nitrogen. By* NORA M. CARMICHAEL, *M.Sc., Musgrave Student in Physics* (1928-29), *The Queen's University of Belfast* †.

[Plate IX.]

1. *Introduction.*

IN a recent communication ‡ a space-charge theory was developed for the primary dark space of a Geissler discharge, which although in accordance with the main experimental data, did not explain satisfactorily its apparent absence in oxygen and nitrogen. It is possible that the primary dark space does exist in these gases as an electrical unit of the discharge (although on any theory it would be extremely thin) but is masked by radiation. In the present investigation we have made a careful re-examination of the light on the immediate surface of the cathode under a variety of conditions. No evidence has been found for the existence of a primary dark space comparable with those present in the inert gases and in hydrogen, but a dark space has been noticed in oxygen at the negative edge of the negative glow maximum which does not appear to have been recorded previously.

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* C. T. Lane and E. S. Bieler, Proc. Roy. Soc. Canada, III. xxii. p. 117 (1928).

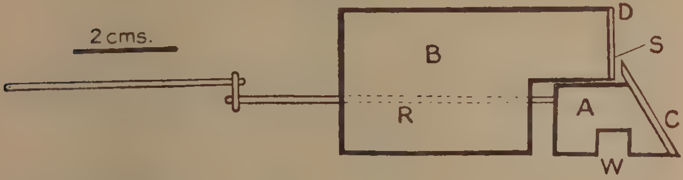
† Communicated by Dr. K. G. Emeléus.

‡ Emeléus and Carmichael, Phil. Mag. v. p. 1039 (1928).

2. *The Primary Dark Space.*

A cathode of the form shown in fig. 1 was used in the first part of the work. It consisted of two parts, A and B, cut from seamless steel tubing 2·9 cm. in diameter. B could be moved freely with a magnet along the two rods R, which were screwed to A, A having a fixed position in the discharge tube. The relative positions of A and B determined both the width of the slit S between the flat surfaces C and D, of polished silver, and the depth of discharge which could be viewed through the gap W. With this cathode, the feeble radiation from the surface of D could be exposed to a spectroscope or a camera for relatively long periods without disturbance due to stray light from the intense radiation from the negative glow. No soldering was used, and the complete electrode was degassed in a vacuum furnace before mounting, together with the anode, a plane disk of nickel.

Fig. 1.



The entire apparatus was baked out under vacuum with a hand blowpipe and allowed to cool. Pure finely divided potassium permanganate was then introduced into a series of small bulbs, liquid air put on to the traps, and the remaining parts baked again. Oxygen was then generated and collected in large glass cylinders. From these it was allowed to stream through one capillary to the discharge tube and was pumped out through a second capillary; by suitable choice of capillaries and with the appropriate pressure in the cylinders a constant pressure was maintained in the discharge tube, a steady stream of pure oxygen being thus obtained. The pressure was measured by a McLeod gauge, protected by a liquid-air trap, and other traps were situated at the immediate entrance and exit of the discharge tube, and in the leads to the cylinders and the pump.

In the case of nitrogen the same baking process was carried out, and nitrogen generated from the explosion of sodium azide, the metallic sodium formed in the reaction assisting in its purification.

The applied potential had a maximum of 450 volts and could be varied by a wire potentiometer.

Pl. IX., *a*, is a typical example of some thirty photographs which were taken of discharges through nitrogen and oxygen. It shows the cathode glow distinctly (CG), but gives no indication of a primary dark space. L is light reflected from the cathode glow by the back surface of C inside S.

After running the tube for a short time a fine line of sputtering developed on the lower surface of the cathode along the line of separation of the parts exposed to and protected from the discharge, which was probably due to back sputtering from the fine edge of C. This may be associated with the observed strong development of the 1S–2P pair of lines of Ag I at 3281 and 3384 A, a result which would point to the above as a possible method for the investigation of the *raies ultimes* of small quantities of metals.

In view of the fact that this radiation from the cathode material was excited in the region we wished to study, the cathode was then replaced by one of simple type, a cylinder of seamless steel with a circle of platinum foil spun on to the plane face exposed to the discharge. The former precautions for purification were again observed. Examples of the resulting photographs are shown in Pl. IX., *c* and *d*, for nitrogen and oxygen respectively. These are deliberately over-exposed for the negative glow (NG), to bring out the cathode glow (CG) distinctly. There is again no indication of a primary dark space. Similar negative results were obtained with a cathode of iron, and have been obtained by Aston with aluminium*.

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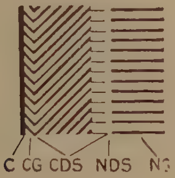
* Aston, Proc. Roy. Soc., lxxx. p. 45 (1908).

3. *A New Dark Space in Oxygen.*

A dark space which does not appear to have been described hitherto was observed in the discharge through oxygen, to the negative side of the curiously sharp edge of the negative glow that is characteristic of the Geissler discharge through this gas. It is intensely black and sharply bounded, features which it is difficult to reproduce in a photograph (Pl. IX., *b*) on account of the concavity of the negative glow surface towards the cathode. Its position is indicated in fig. 2. Its thickness (d) as estimated with a cathetometer appears to follow the law that dV/D is constant, which holds for the primary dark space where V is the cathode fall in potential and D the thickness of the cathode dark space. It is also thicker towards the periphery of the tube, where the current density is less than at the axis. d is difficult to measure accurately, again because of the concavity of the negative glow, but some idea of its order of magnitude will be obtained from the following table :—

Fig. 2.



Thickness of new dark space	0·23 mm.
Thickness of cathode dark space . .	4·5 mm.
Cathode fall in potential	420 volts.
Gas pressure	1 mm. Hg.
Current density (average over cathode)	0·18 mA/cm.^{2}
Cathode of platinum.	

An attempt has been made to investigate this dark space by the Langmuir method of exploring electrodes in a simple tube of the type used by Emeléus and Harris *. The collector was a fine molybdenum wire of effective length 0·3 cm. and 0·1 mm. diameter. The usual precautions were taken to ensure purity of the gas, and two large cylinders were put in connexion with the tube to minimize changes in pressure. Characteristic curves were taken in the usual way. There is some doubt as to the exact interpretation to be put upon collector characteristics for the more negative parts of this section of the discharge, but the usual curves were obtained to the positive side of the new dark space, and the anomalous cathode dark space type to its negative side. We can therefore regard the new dark space as a *region* in which the transition from the negative glow to the cathode dark space takes place, this conclusion being compatible with some measurements by W. L. Brown and E. E. Thomson made on the shadows thrown by collectors in the cathode dark space, details of which will be published shortly. The electron concentrations in the negative glow were of the usual order, but the electron temperatures were decidedly low, 0·5 volt and 1·8 volts being typical numbers for the two groups present in the middle of the negative glow in a 450 volt discharge at 0·5 mm. Hg.

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* Emeléus and Harris, Phil. Mag. iv. p. 49 (1927).

Seeliger * has shown that it is necessary to proceed with great caution in interpreting the visual appearance presented by a discharge. In this particular instance the dark space remained unaltered in position, and lost none of its sharpness when viewed through a range of Wratten colour filters. The other possibility, that it is a contrast effect, is disposed of by its appearance on a photometric record of one of our less good plates.

The integrated colour of the light from each side of this dark space is the greenish white of the oxygen discharge, although it is naturally very feeble to its negative side, fading off rapidly into the violet of the cathode dark space proper. A study of the individual lines and bands in the discharge was made by the subjective method of Seeliger †. The discharge tube was mounted vertically and a fine black thread tied round it at the level of the new dark space. An image of the discharge was focussed on the slit of a Hilger constant deviation spectrometer, and the relative intensities in the spectrum on either side of the image of the thread noted. Several lines due to the excitation of sputtering metal atoms came up intensely at the cathode surface, and faded out towards the negative glow. The dark line of the image of the thread which marked the position of the new dark space coincided with the region of rapid fall in intensity of the ozone bands already recorded by Seeliger and Lindow [*]. and with the region of rapid fall in intensity of the green and red negative bands of oxygen, but some light due to both of these still persisted faintly to its negative side. The arc lines (O I) and spark lines (O II) of atomic oxygen showed a somewhat less rapid change in intensity, again in agreement with Seeliger's results.

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* Seeliger and Lindow, *Phys. Zeits.* xxvi. p. 393 (1925).

† *Loc. cit.*

Taking Seeliger's observations in conjunction with ours, particularly those made with an exploring electrode, we conclude that a very large number of the ions in the negative glow are probably molecular oxygen O_2^+ rather than atomic oxygen O^+. The positive ray analysis of Hogness and Lunn would suggest a ratio of the former to the latter of about seven to one [†].

A search has again been made in other gases (nitrogen, oxygen, hydrogen, argon, neon) for this dark space, so far with negative results.

4. *Origin of the Dark Space.*

Our observations very strongly suggest that the new dark space is an ionic sheath, in this case separating two parts of the discharge instead of an electrode and the discharge. Other evidence for the existence of a sheath between different regions of an ionized gas would appear to be contained in some of the observations made by J. J. Thomson [‡] on the electrodeless discharge. The sheath is almost certainly one of positive ions, and its existence is compatible with Morse's theory of the cathode dark space [§], which seems to allow of a rather abrupt transition from a moderately large field in the cathode dark space to practically zero field in the negative glow. Brown and Thomson (see above) have obtained experimental evidence for the existence of this fairly sharp transition. Interpreting it in terms of Poisson's relation, there should be present there a sheath of rather denser positive electricity than in neighbouring parts of the cathode dark space. In the case of argon there is independent evidence that there is an additional region of excess positive space charge in the negative side of the negative glow from the work of Emeléus and Harris *, who suggested that it existed to counteract the effects of diffusion from the intense ionization of the middle of the negative glow in this gas. No dark sheath has been observed in argon, but conversely our analysis with exploring electrodes has shown that the negative glow is much more nearly equipotential in oxygen than in argon (under the conditions mentioned in the last section it is equipotential to within 1·5 volts between the new dark space and the Faraday dark space), and has its maximum of ionization closer to its negative boundary, suggesting that the relative extents of the reversed field in the negative glow and the new dark space, if these can be associated with one another, are determined by the large mobility of electrons in argon, as compared with their small mobility in oxygen. If this is so, the dark space might be visible in the discharge through gases such as chlorine. A more detailed investigation of this part of the discharge in several gases has been planned, which it is hoped will decide these questions.

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[*] *Loc. cit.*

[†] Hogness and Lunn, Phys. Rev. xxvii. p. 732 (1926).

[‡] J. J. Thomson, Phil. Mag. iv. p. 1128 (1927).

[§] Morse, Phys. Rev. xxxi. p. 1003 (1928).

Summary.

A search has been made for a primary dark space in the Geissler discharges through oxygen and nitrogen, with negative results. A new dark space has been described in oxygen between the negative glow and cathode dark space, which appears to be a positive ion sheath between these two regions of the discharge.

I should like to thank Prof. J. Milroy for the loan of a Hilger constant deviation spectrometer; Mr. E. E. Thomson for assistance in some of the photography; Dr. S. W. J. Childs, of King's College, London, for photometring one of the plates; and Dr. Emeléus, for his help throughout the investigation and in the preparation of this paper.

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* Emeléus and Harris, *loc. cit.*

XLII. *The Relation between Raman Lines and Infra-red Bands.* *By* C. P. Snow (*Keddey Fletcher-Warr Student*) *.

Introduction.

QUESTIONS of technique have hampered the growth of the theory of the Raman effect in a way which has not been fully realized. The discovery was made in liquids like carbon tetrachloride, toluene, and benzene; and, because the effect was observed most readily in such substances, attention was kept upon them. The result was that no comparison could be made between the Raman scattering due to a molecule and the detail of its infra-red absorption, for the bands of toluene or benzene are beyond the powers, both theoretical and practical, of present-day analysis.

Accordingly, the agreement of the position of known gross infra-red bands with the amount of scattering ($\delta\nu$) of some Raman lines was taken as proof of the simplest possible theory—that of Smekal, in which the molecule is supposed to absorb or emit a quantum $h\nu$, where ν is a characteristic infra-red frequency, usually of a vibration band. It was necessary to ignore the non-appearance of Raman lines corresponding to strong absorption bands, and the appearance of lines which had no corresponding bands at all.

These unexplained exceptions were soon reinforced by the results of experiments upon gases with well-known infra-red spectra; and it became clear that R. W. Wood's (1) work on hydrogen chloride and Rasetti's (2) on carbon dioxide made the existing theory inadequate. Langer (3) and Dieke (4) have now shown that the Kramers theory of dispersion includes, implicity, the theory of the Raman effect, and that these apparently anomalous results follow naturally from it. It predicts that the shifts of the Raman lines from the unmodified exciting line are equal to differences of excited levels of the molecule, where the excited levels themselves have a common ground-level. The intensity of any Raman line depends upon the transition coefficients from the common level of the two appropriate excited levels; Langer has derived the expression

$$\mathrm{A}_{kn}\,\mathrm{A}_{ln}\left[\frac{1}{\nu_2+\nu_{kn}}+\frac{1}{\nu\pm\nu_{ln}}\right](\nu\pm\nu_{kl})^2,$$

the square of which represents the intensity of the transition

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* Communicated by Dr. Eric K. Rideal.

ν_{kl} *i.e.* $\nu_k-\nu_l$. A_{kn} describes the intensity of the transition of ν_{kn}, and is $\int r\psi_k\psi_n dx$.

Langer has shown the completeness with which this theory accounts for the Raman lines of carbon tetrachloride; and Dieke has given a convincing reason for the "missing line" of hydrogen chloride which was found by Wood. It is the writer's aim to make clear the application of the theory to some molecules for which there is considerable spectroscopic data, and to add a little lately acquired infra-red evidence.

I. OXYGEN AND NITROGEN.

Raman observations.

McLennan and McLeod (5) found that the Raman effect in liquid oxygen and nitrogen gives lines corresponding to the frequencies:—

for oxygen	1552	1551	3049
for nitrogen	2335	2322	4632

In their paper they mention that there are no infra-red bands due to O_2 or N_2, since the molecules are symmetrical and have no electric moment. Their suggestion is that in the liquid state there exists a mutual polarization, with the formation of weak dipoles (this must be the case in liquid sulphur, where the dipole $\overset{+}{S}-\overset{-}{S}$ is certainly present).

The actual process is likely to be the formation of quadripoles, which behave optically like dipoles to a first approximation.

Possible existence of infra-red bands of oxygen and nitrogen in the gaseous state.

Several considerations made it appear conceivable that gaseous oxygen and nitrogen might have vibration-rotation bands. They were

(i.) That the complete symmetry of O_2 and N_2 usually assumed is not proved, nor is there any other case (except perhaps I_2) known.

(ii.) That the emission curve of a Nernst glower or similar source shows irregularities, some of which are due to the absorption by carbon dioxide and water of the atmosphere; near to the carbon dioxide and water bands there are small dips at frequencies much the same as McLennan and McLeod's. It must be borne in mind that these also may be caused by CO_2 and H_2O.

(iii.) That Coblentz ⁽⁶⁾ attributed absorption at 3·2 μ (3100 cm.$^{-1}$) to oxygen, after considering the possibility of its being due to water.

(iv.) That Sleator ⁽⁷⁾, when determining the absorption of water at 2·6 μ, plotted bands which did not diminish when the amount of water in the absorbing system was lessened.

Hence (ii.) was investigated more fully. There was at hand a convenient instrument for the purpose, already described by A. M. Taylor and E. K. Rideal ⁽⁸⁾. It is a small Hilger infra-red spectrometer, encased in a cast iron safe in order to protect the thermopile from disturbances caused by adiabatic expansion and contraction of the air. This made it easy to obtain a vacuum spectrometer, for a thorough covering of the outside with Chatterton's compound was all that was necessary. Inside the safe dishes containing sticks of potassium hydrate were placed; outside, the Nernst and mirrors were so arranged as to make the path of the radiation through air quite small. The air path was enclosed in a funnel made of sheet brass and lined with dishes of stick potassium hydrate.

The safe was evacuated, and the emission curve of the Nernst glower plotted. Two portions of the curve are shown in figs. 1 and 2; comparison with the ordinary emission curve in air emphasises the smoothing out of the dips due to absorption by carbon dioxide and water. The flatness in fig. 1 is probably caused by a little water vapour persisting in the system despite all precautions.

Oxygen was pumped in at an atmosphere's pressure, and the curve between 5·9 and 6·8 μ plotted. The result is seen in fig. 1, and the curve in the neighbourhood of 4 μ with nitrogen at an atmosphere's pressure in the instrument is given in fig. 3. A rock-salt prism cannot profitably be used from 2–3·5 μ, and so the curve at higher frequencies could not be obtained with any accuracy; it was obviously impossible to evacuate the high dispersion instrument recently described ⁽¹⁰⁾.

The curves suggest a small but definite absorption by oxygen and possibly by nitrogen. The effect was reproducible, qualitatively at least. However, it must be remembered that even for oxygen the effect is very small;

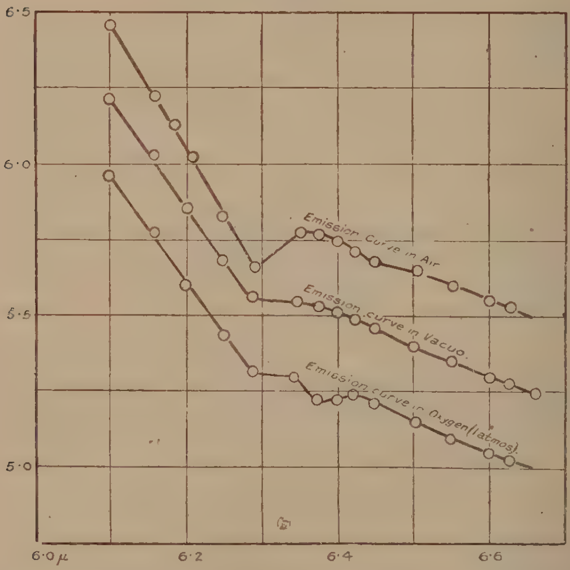
the complication introduced by the nearby bands of water and carbon dioxide is another factor which makes a definite claim unjustifiable. On the other hand, a precise and deciding test seems forbidden by the nature of the problem.

The frequencies of the possible bands are :—

oxygen	c. 1540 cm.$^{-1}$.
nitrogen	c. 2320 cm.$^{-1}$.

The conflict of their occurring with the inference from electric moment measurements is not serious, although the delicate method of Stuart (9) has confirmed previous work in giving a zero moment for both molecules. An effect of the magnitude observed would only require a moment of the order of 5 . 10^{-20} e. s. u.

Fig. 1.

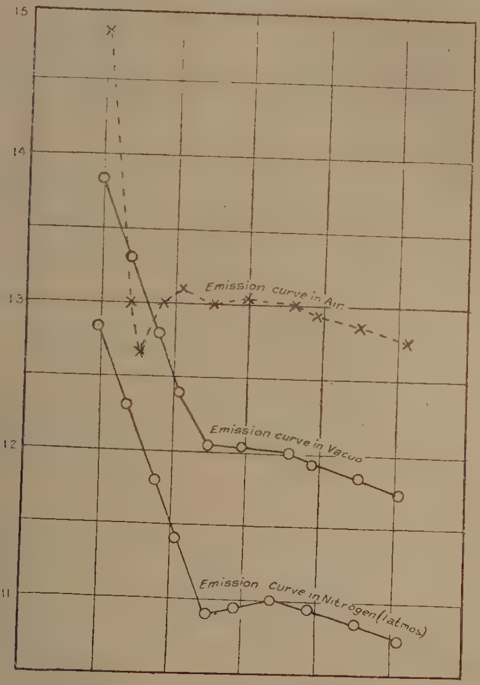


Explanation of Raman lines of oxygen and nitrogen.

The general statement may be made, tentatively, that the Raman lines observed by McLennan and McLeod correspond to infra-red frequencies of the molecules both in the liquid and in the gaseous state. The important result—which cannot be questioned—is that here the vibration frequency deduced from the Raman effect is not a difference frequency but a normal frequency of the molecule.

This must be the case if a diatomic molecule is to show any Raman shifts; Dieke has shown how the Kramers theory includes difference terms between rotational states. If (i, j) represents a molecule in its first excited vibrational state and its jth rotational state, then $(i, j-0, j_1)$ can under certain conditions be a Raman transition. The conditions obviously are $j=j_1$ or, alternatively, $j=j_1 \pm 2$. The predicted Raman lines are then a strong line corresponding to the centre or rotationless state of the infra-red vibration-rotation band, and weak lines at twice the separations of the infra-red bands (rotation bands). In Wood's case the dispersion was high enough to give this arrangement.

Fig. 2.



There is little doubt that the oxygen and nitrogen Raman lines would show a similar structure under high dispersion. It would be particularly interesting to see the convergence that can be prophesied on the low frequency side of the central line; and the intensity relationships of fundamental and overtone would be of value. The comparison of the ratio of the intensities of the Raman fundamental and overtone with the ratio of the intensities of the infra-red bands (they could be calculated for O_2 and N_2, and are known for CO) would act as a final proof of the correctness of the Lange-Dieke explanation.

There is some evidence already for this view. The position of the centre of an infra-red band can be calculated from electronic band spectra data. This has recently been shown to be true for both NO and CO (see later). To a close approximation, the centres of the infra-red band so calculated agree with McLennan and McLeod's figures for the Raman lines. Now, the oxygen and nitrogen bands in the infra-red, actual or hypothetical, must be very like the HCl or CO bands, and have no central line. That is, the Smekal theory would suggest two or more Raman lines arranged symmetrically about a missing central line. On the other band, the new explanation would give, as a first effect, one central line.

	w_0 (electronic bands).	$w_0(1-x)$. Calculated centre of infra-red band.	Raman, Mc & McL.	Theoretical Raman, upon Smekal Theory.
O_2...	2165	2154	2152	Two lines, ca. 2151 and 2157
N_2...	2345	2331	2329	Two lines, ca. 2327 and 2335

II. CARBON MONOXIDE.

Rasetti observed a Raman line for carbon monoxide which shows a surprisingly close resemblance to the w_0 of the electronic bands of CO. This can scarcely be the case; with more accurate measurement, it is certain that the line corresponds to the centre of the infra-red band $w_0(1-x)$. Recent work (11) upon NO and CO has shown quite definitely that the centre of the infra-red band is described by this value: the relevant figures, together with Rasetti's Raman effect result, are given below:—

	w_0(electronic band spectra).	$w_0(1-x)$ [calculated].	Centre of infra-red band.	Raman.
NO......	1892	1878	1883	—
CO......	2155	2142	2144	2155

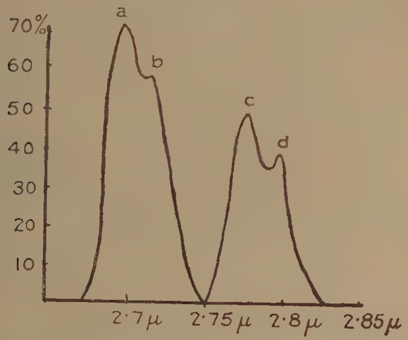
In every other way the Dieke explanation seems to hold; it is significant from the point of view of intensity that the overtone has not yet been detected in the Raman effect.

III. CARBON DIOXIDE.

Rasetti's result for gaseous carbon dioxide is an interesting example of the truth of the Kramers prediction. The infrared bands at 2·74 $\mu(\nu_2)$ and 4·25 $\mu(\nu_1)$ are drawn roughly in **fig. 3.**

ν_1 represents a vibration of the carbon atom perpendicular to the symmetry axis, and ν_2 one of the vibrations of the carbon atom parallel to it. Accordingly, they have a ground level, the unexcited state of the molecule; and a transition between them is predicted by the Kramers theory. Actually, Rasetti observed two lines at $\partial\nu=1392$ cm.$^{-1}$ and $\partial\nu=1284$ cm.$^{-1}$. The difference between *a* and *e* is 1368 cm.$^{-1}$, between *c* and *f* 1295 cm.$^{-1}$.

Fig. 3.



The justification for this apparently arbitrary potentially, a number of Raman lines corresponding to the vibrational transition $\nu_2-\nu_1$ and to various transitions in rotational quantum number. To a first approximation, the difference between the maxima of the R branches will be the strongest Raman line, with the difference between the maxima of the P branches of the same order of intensity. As Rasetti's photograph was taken under circumstances likely to give only the strongest lines, it was a qualitative test of intensity; and the lines given by it may be looked upon as molecular "raies ultimes."

The correspondence of the frequency differences with the theoretical is fairly satisfactory. Rasetti himself, before the difference term was accepted as the normal Raman effect, noticed that the Raman lines were numerically very close to the differences of the maxima of the $4{\cdot}25\,\mu$ band and the centres of the double doublet at $2{\cdot}74\,\mu$. His calculated differences are nearer to the observed fact than those taken as above; this seems to be due to the use of figures for the $4{\cdot}25\,\mu$ band given by Schaefer and Phillips (12). Their paper contains the misprint 4·255 (instead of 4·225) for the maximum of the R branch of the doublet. If the correct value is used, the differences taken in Rasetti's way do not agree with the Raman shifts as nearly as do the differences of the maxima.

It may be noticed that almost exact agreement with experiment can be obtained by subtracting the low frequency band of the $4{\cdot}25\,\mu$ doublet from the two maxima *a* and *c*, of the double doublet. This does not seem legitimate, and it would involve, in any case, complicated selection rules. The difference of the maxima is the obvious course with the present data.

Some puzzling numerical relationships derived by C. R. Bailey (13) may be discussed briefly, as their acceptance as a representation of an unknown law would imply a more involved explanation of the Raman effect.

The energy expression for a rotator with two effective moments of inertia (the two large moments in CO_2 are nearly equal) is

$$E_r=\left[\frac{m(m+1)}{C}+\left(\frac{1}{A}-\frac{1}{C}\right)s^2\right]\frac{h^2}{8\pi^2}$$

(or, for simplicity, the older form)

$$E_r=\left[\frac{m^2}{C}+\left(\frac{1}{A}-\frac{1}{C}\right)s^2\right]\frac{h^2}{8\pi^2}$$

in ν_1, the selection rules apply

$$\Delta m=\pm 1,$$

$$\Delta s=0.$$

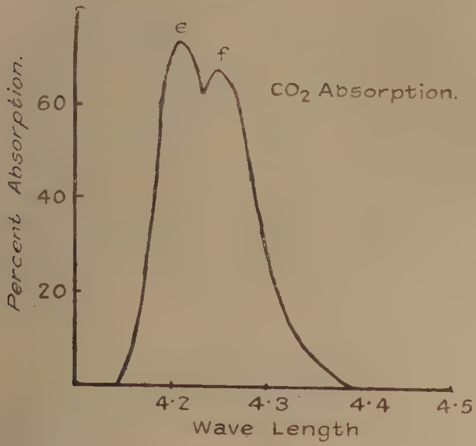
Accordingly, the doublet shown in fig. 3 *a* is exactly like the band system of a diatomic molecule of moment of inertia C. The separation of the lines (at present unresolved) is $\frac{h}{4\pi^2 C}$. The separation of the doublet is described approximately by the Bjerrum classical expression. It is of the order of 30 cm.$^{-1}$.

The band at 2·74 μ depends upon the selection rules

$$\Delta m = 0_1 \pm 1, \quad \Delta s = 1,$$

and can be divided into two systems of lines

Fig. 3*a*.



I. . . . . . . $$\partial\nu = \left(\frac{1}{A} - \frac{1}{C}\right)\frac{h}{4\pi^2}$$

(the four large bands of the double doublet belong to this system),

II. . . . . $$\partial\nu = \frac{h}{4\pi^2 C}$$

(these lines give a fine structure to the lines of I). The simplification happens that the maxima of the Bjerrum doublets coincide with the tops of the bands of I. *I. e.* the separation

$$\left(\frac{1}{A} - \frac{1}{C}\right)\frac{h}{4\pi^2} \overset{\frown}{=} 30 \text{ cm.}^{-1}.$$

The separation

$$b - c = \left(\frac{1}{A} - \frac{1}{C}\right)\frac{h}{2\pi^2},$$

as, for example, in HCl, for there appears to be no Q branch. The numerical value of it is 70 cm.$^{-1}$; there is an irregularity which may vanish with more exact measurement.

Bailey's series depend upon the separation of the bands a and c in ν_2—the two more intense members of the doublets. He finds that half this separation is a constantly occurring frequency in CO_2 bands. As he says, it is difficult to see any reason for this. It is not surprising that the separation itself is common, for it is roughly three times the separation of the Bjerrum doublet where the fine structure is $\frac{h}{4\pi^2 C}$ $\Big($and, of course, three times the band separation $\partial\nu = \left(\frac{1}{A} - \frac{1}{C}\right)\cdot\frac{h}{4\pi^2}\Big)$. But half this separation would seem physically meaningless.

It is possible that the fine structure of the four large bands of the 2·74 μ band may show that the superposition of the band systems is not so perfect as has been assumed; the problem has, however, the experimental difficulty that the separations of the fine structure will be of the order of one wave number.

IV. Hydrogen.

The Raman lines of hydrogen at the moment have not been reconciled to the Langer-Dieke scheme. H. S. Allen⁽¹⁴⁾, from a study of the "many lines" spectrum, found results which are not consistent with those of McLennan and McLeod, from the direct effect in liquid hydrogen; and neither of the sets of observations fits the theory well.

The adoption of Dieke's selection rule $j = j \pm 2$ means that the apparent beautiful confirmation in McLennan and McLeod's paper of the existence of symmetrical and antisymmetrical states of hydrogen cannot be retained, and the two lines detected by them should be of similar origin to the lines found by Wood on each side of the "missing line." If this were the case, it seems necessary that there should be a strongly marked difference in intensities between the two lines, as the alternation in intensity of the H_2 bands should persist. This does not appear to be verified by the experiment.

As hydrogen gives the most important difficulty, mention did not seem worthless, although the writer can offer no constructive suggestion.

Summary.

(i.) The Langer-Dieke account of the relation between Raman lines and infra-red bands is discussed.

(ii.) It is pointed out that for O_2, N_2, and CO a similar scheme to that proposed by Dieke for HCl must be used; and that, in all three cases, the position of the central Raman line should not coincide with the electronic vibration frequency.

(iii.) There is some experimental evidence for the existence of vibration-rotation bands of oxygen and nitrogen. Work with an infra-red vacuum spectrometer leads to the view that absorption by oxygen, while not definitely proved, is more than a possibility. The intensity of absorption for a metre path of oxygen has 5 per cent. as its upper limit.

(iv.) The agreement of the Raman effect for CO_2 with the Langer-Dieke account is stressed, and some suggestions are advanced upon the transitions to be expected.

(v.) The Raman effect for H_2 gives results which are not yet explained by the Langer-Dieke theory.

Acknowledgments.

I should like to give my thanks to Dr. A. M. Taylor, for advice and help, particularly in the use of the vacuum spectrometer; to Mr. F. I. G. Rawlins, who led me through the difficulties of the carbon dioxide question; to Mr. A. C. Menzies, of University College, Leicester, for many stimulating conversations; to Dr. E. K. Rideal, for interest and criticism, and for communicating the paper. Finally, I should like to state my continued gratitude to the Keddey Fletcher-Warr Studentship Board.

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XLIII. *Intensively Dried Liquids.*
By John William Smith, *B.Sc., Ph.D.*[*]

IT has been shown recently by Lenher [†] that the method used by Baker [‡] and by Smits [§] for the determination of the boiling-points of their intensively dried liquids may lead to superheating, yielding high values up to 27° above the normal boiling point even when ordinary pure, but undried, liquids are used. Hence it is claimed that such superheating may well account for Baker's boiling-point changes, which, therefore, are inconclusive in establishing a change in the internal state of the liquids. This discovery is extremely important, but it does not explain by any means all the phenomena observed with intensively dried liquids, and therefore must by no means be regarded as putting an end to this branch of chemistry.

The best established fact concerning intensively dried systems is their slowness in attaining the equilibrium state after any disturbance of the latter. For example, after a sudden change in temperature, dried liquids require a very considerably longer period than moist liquids in order to reach a steady vapour pressure [||]. The same phenomenon is observed after rapidly distilling a portion of the liquid away [¶]. Dry sulphur trioxide exhibits these phenomena much more conspicuously even than dry liquids [**]. As has been pointed out by Smits [††], this slowness in behaviour may well be the cause of the very high vapour densities found by Baker for several liquids [‡‡], and for the abnormal latent heat found in the case of intensively dried benzene. Thus there is a good deal of fundamental evidence, mainly from the work of Baker, that there is some important change in the behaviour of liquids after intensive drying, though his view that there is a very large change in the molecular complexity does not seem to be supported on very firm grounds. Baker's measurements have always been made in what may be described as dynamic systems, in which the readings may have been taken before equilibrium has had time to establish itself, owing to the fear of rapid reversion to the normal state, the result being that large differences were found between the physical properties of the moist and dry liquids. On the other hand, other observers have measured static properties, *e. g.*, the change of the vapour pressure at the drying temperature, but the changes found have been small, in no way comparable with the large effects observed by Baker.

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[*] Communicated by Prof. F. G. Donnan, F.R.S.

[†] 'Nature,' cxxiii, p. 907 (1929).

[‡] Journ. Chem. Soc. cxxi. p. 568 (1922).

[§] Journ. Chem. Soc. cxxv. p. 1069 (1924).

[||] J. W. Smith, Journ. Chem. Soc. p. 867 (1927).

[¶] Smits, de Liefde, Swart, and Claassen, Journ. Chem. Soc. p. 2657 (1926).

[**] Smits and Schoenmaker, Journ. Chem. Soc. cxxv. p. 2554 (1924); p. 1108 (1926).

[††] Journ. Chem. Soc. p. 2399 (1928).

[‡‡] Journ. Chem. Soc. p. 1051 (1928).

The slowing down of the rate of attainment of equilibrium in liquids seems to be quite parallel to the gradual slowing down of the velocity of many chemical reactions on the removal of water-vapour, and doubtless when a satisfactory explanation is found for the one it will apply to the other case also.

This slowness in the attainment of equilibrium may well account for the fact that Alex. Smith and Menzies* found that dry calomel exerted no vapour pressure at all, since during the brief period during which they heated the calomel (a quarter of an hour) before sealing off the large bulb containing the vapour, it is probable that the vaporization of the dry specimen would be very slight indeed, although the same period of heating may well have sufficed for the undried specimen under analogous conditions. Similar, but not so marked, effects have been observed recently by Rodebush and Michalek † in measurements of the vapour pressure and vapour density of ammonium chloride.

Having the criticism from Smits on the one hand ‡ that Baker's surface tension measurements are not true indications of a change in the inner complexity of the system, and from Lenher § on the other that the boiling-point determinations are inconclusive, there no longer remains any certain evidence in favour of perhaps the most surprising phenomenon indicated by Baker's experiments, that is, that liquids retained their abnormal "dry" properties for some time after contact with moisture. This property, indeed, seems to have been relied upon by Lenher to enable him to complete his measurements before any considerable change in his "dry" liquids could occur. It now seems much more rational to suppose that, like the gaseous systems referred to above, the "dry" liquids will be extremely sensitive to very small traces of water-vapour and will revert to their normal behaviour almost immediately on contact with moist air or moist apparatus. Thus Lenher's experiments, using the boiling-point apparatus with a platinum wire heating element, do not prove conclusively that there was no abnormality in the liquid before the drying tube was opened, since no care was taken to avoid contact with moist air after opening the tubes.

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* *Zeits. phys. Chem.* lxxvi. p. 713 (1911).

† Journ. Amer. Chem. Soc. li. p. 748 (1929).

‡ Journ. Chem. Soc. cxxv. p. 2399 (1928).

§ 'Nature,' cxxiii. p. 907 (1929).

The drying effect, if it is primarily a slowing down of the inner transformations, may well occur in quite the early stages of the usual long intensive drying process. Thus, in the author's experiments with nitrogen tetroxide, during the first few days after sealing the apparatus the liquid could be distilled over completely between two bulbs, one at 0° C. and the other at about 18° C., through a phosphorus pentoxide *U*-tube, in the course of about three hours. This period, however, increased gradually till over five hours were required for a complete distillation to be carried out under comparable conditions. The greater part of this slowing down of the rate of distillation occurred during the first month or two. The effect was not due to the compression of the phosphorus pentoxide column, since after moist air had been admitted to the apparatus and the latter re-evacuated and sealed off again with very little loss of the nitrogen tetroxide, the former three hour period was restored. Now, after a further two and a half years without any repeated distillation the time required is again much greater under the same conditions as before, being about six hours. It is proposed to carry out further experiments on the effect of drying on the rate of distillation of liquids.

Another recent communication which is of considerable interest in this connexion is that by Manley *, who has found that the specific volume of benzene in the presence of phosphorus pentoxide is dependent on the temperature to which the benzene has been exposed before a determination is carried out, being diminished by previous cooling, and increased when the liquid has first been heated. He attributes the effect of cooling to the ejection of water from the benzene, and that of heating to the absorption of moisture from the metaphosphoric acid previously formed. It is quite possible, however, that this is only yet another example of the "slow" behaviour of dried liquids, some time being required for the inner equilibrium to be established after disturbance by temperature change.

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* 'Nature,' cxxiii. p. 907 (1929).

In conclusion the author desires to express his indebtedness to Professor F. G. Donnan, F.R.S., for his helpful advice and criticism.

Sir William Ramsay Laboratories of
Inorganic and Physical Chemistry,
University College, London.
July, 1929.

XLIV. *The Spectrum of the Negative Glow in Oxygen.* *By* K. G. Emeléus, *M.A.*, *Ph.D.*, *and* Florence M. Emeléus, *M.Sc.*, *Department of Physics, The Queen's University of Belfast* [*].

1. *Introduction.*

MUCH work has been done lately on the interpretation of spectra associated with oxygen. In particular, the lines of the first spark spectrum of the atom (OII) have been catalogued and extensively analysed by A .Fowler [†], H. N. Russell [‡], R. H. Fowler and Hartree [§], and Mihul [||], and the lines of O III have been examined by A. Fowler [¶] and others.

The negative glow in oxygen is a good source of band spectra, arc lines and the lower spark lines, affording, in fact, probably the most gentle method available for the production of the latter.

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[*] Communicated by the Authors.

[†] A. Fowler, Proc. Roy. Soc. cx. p. 476 (1926).

[‡] H. N. Russell, Phys. Rev. xxxi. p. 27 (1928).

[§] R. H. Fowler and Hartree, Proc. Roy. Soc. cxi. p. 83 (1926).

[||] Mihul, *Annales de Physique*, ix. p. 261 (1928).

[¶] A. Fowler, Proc. Roy. Soc. cxvii. p. 317 (1928).

A valuable partial photometric study of the negative glow for the visible region has been made by Seeliger and Lindow *. The present paper includes a more complete description of the spectrum of the negative glow, and an examination of the extent to which its production can be explained in the light of recent work upon the electrical conditions obtaining there.

2. *Apparatus and Results.*

The discharge tube used was originally designed for absorption work, and was similar to one referred to by Paschen †. It was 95 cm. long and 5·5 cm. in diameter, with the ends closed by metal caps, holding quartz windows, the leads to the electrodes, and a tube connecting with the pumping train. The electrodes consisted of rectangular sheets of degassed nickel, 65 cm. × 3·5 cm., supported in the tube on a framework of glass rods. The ends of the tube were sealed with picein. Oxygen was generated from potassium permanganate, and water and carbon vapours were removed by phosphorus pentoxide and caustic potash. The tube was protected by a pair of liquid air traps from tap-grease vapour, and from mercury vapour from the diffusion pump and McLeod gauge. The discharge was run off the 440 volt D.C. mains, at pressures of about 0·5 mm. Hg., and current densities of some 1-2 $m\text{A/cm.}^2$ The negative glow occupied the middle of the tube, and there was present for part of the time a relatively feeble anode glow covering the whole of the anode.

The spectroscopes used were :—

(i) A glass prism instrument for the visible and infra-red, having a dispersion of 20 A per mm. at λ 4300, and 200 A per mm. at λ 8000.

(ii) A medium quartz prism instrument with a dispersion of 6 A per mm. at λ 2300, and 16 A per mm. at λ 3000.

(iii) A Hilger E 31 small quartz spectrometer for the ultraviolet below λ 2200.

Oiled plates were used for (iii), and Kodak special infra-red plates for the longer wave-lengths with (i).

The negative glow was viewed end-on through a quartz window, the times of exposure being usually 8 hrs. for the visible, 25 hrs. for the ultraviolet and 50 hours for the infra-red. There was little radiation below λ 2200, except immediately after the tube was set up, when the carbon line at λ 1930 came up strongly. This had disappeared after running the tube continuously for a fortnight with repeated renewals of gas, and ultimately the only foreign spectra were the bands at λ 2882 and λ 2895 which have been attributed to carbon dioxide [*], and these only appeared faintly.

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* Seeliger and Lindow, *Phys. Zeits.* xxvi. p. 393 (1925).

† Paschen, *Ann. d. Phys.* xlv. p. 625 (1914).

The following spectra were present.—

(1) The visible and ultraviolet negative bands of oxygen, the latter being decidedly less intense relative to the line spectrum than on the plates obtained by R. C. Johnson, with a condensed discharge [†].

(2) The violet ozone bands, again less intense than on Johnson's plates.

(3) All the strongest lines of nickel (Ni I) listed by Kayser [‡] between λ 4000 and λ 2900, without anomalies in relative intensity. These were due to the sputtering material of the electrode.

(4) The two lines of Ni II at λ 2546 ($a^2F_3'-a^2G_4'$) and λ 2511 ($a^2F_4'-a^2G_5'$) [§], feebly.

(5) The O III lines at λ 3760 ($3s^3P_2-3p^3\,D_3$), λ 3754 ($3s^3P_1-3p^3D_2$) and λ 3299 ($3s^3P_0-3p^3S_1$), rather feebly [‖]. Other may have been present in small intensity, but obscured by bands.

(6) All the strong lines of O I of wave-length less than λ 8000—the limit of our instruments—in about the relative intensities given by Kayser. λ 5577, if present, could not be resolved from the fine structure of the green oxygen band.

(7) The O II spectrum, to which special interest attaches. With a few exceptions most previously listed lines between λ 4674 and λ 2300 have been found on our plates. The missing lines are mainly those whose intensities have been previously given as (O) or (1), and, it is anticipated, these

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[*] Fox, Duffendack, and Barker, Proc. Nat. Acad. Sci. xiii. p. 302 (1927).

[†] R. C. Johnson, Proc. Roy. Soc. cv. p. 683 (1924).

[‡] Kayser, *Hauptlinien d. Linienpektra.*

[§] Shenstone, Phys. Rev. xxx. p. 255 (1927).

[‖] Fowler, Proc. Roy. Soc. cxvii. p. 317 (1928).

would have appeared on more prolonged exposure. The multiplets $(b, c)^2D'_{2,3}-(c, d)^2D_{2,3}$ were however definitely absent in all cases, and include strong lines which could not have been overlooked. Mr. E. M. Lindsay has verified for us that they appear in the spark between carbon poles in oxygen, so that it is unlikely that their absence is connected with the small trace of carbon present in our tube. We have also checked v. Wijk's observation of the visible lines with a silver spark in oxygen *. There is little room for doubt that they have been correctly assigned, particularly in view of Mihul's examination of the Zeeman effect of the strongest visible lines †. Moreover, Dingle finds corresponding lines in the second spark spectrum of Fluorine (F III)‡, although, as he points out, a number of expected combinations in O II and F III are absent. v. Wijk's investigation of the intensities of the multiplets missing on our plates is unfortunately incomplete. The lines comprise all possible transitions between the D and D′ terms arising from the s^2p^23p and s^2p^23d configurations of the oxygen ion. Apart from these, the relative intensities are about the same as described previously.

(8) A careful search has been made for the prominent lines of O IV, with negative results.

The arc and spark spectra O I and O II, and the negative bands are of comparable intensities. Although the light examined came from the whole of the negative glow, yet Seeliger and Lindow's work shows that it must have come preponderantly from its visually brightest part, which is also where the electrical analysis (below) has shown that the ionic concentrations are greatest.

3. *Correlation of Discharge and Spectroscopic Data.*

The properties of the oxygen atom and molecule are now sufficiently well known to permit of some correlation of the spectrum of the negative glow with the discharge conditions. The latter have been investigated by N. M.

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* v. Wijk, *Zeits. f. Phys.* xlvii. p. 622 (1928).

† Mihul, *loc. cit.*

‡ Dingle, Proc. Roy. Soc. cxxii. p. 153 (1929).

Carmichael[*] in another connexion. Wrede[†] has shown that there is considerable dissociation into atoms in the oxygen discharge; from the ionic concentrations found in the work of Miss Carmichael, most of the atoms present must be neutral. We shall neglect their presence at first, and examine later the consequences of supposing that 10 per cent. of the gas content was atomic oxygen. Judging from Wrede's observations, fewer atoms would probably have been present. Atoms tend to accumulate in large numbers, because, unlike ions, they are not removed in the electric field.

The oxygen molecule (O_2) has a critical potential at about 8 volts, which probably corresponds to dissociation of the molecule into two neutral atoms[‡]. The relevant data concerning ionization of the molecule are contained in the two equations[§]

$$O_2 = O_2^+ + e \quad -15 \text{ volts, and}$$
$$O_2 = O^+ + O + e - 21 \text{ volts.}$$

Oxygen atoms can thus be produced by at least two distinct processes.

The negative bands of oxygen originate in the ionized molecule O_2^+[‖].

The resonance potential of atomic oxygen is 9·1 volts and its ionization potential 13·6 volts[¶]. The ionization potential of singly ionized oxygen is 35 volts[**] and that of doubly ionized oxygen 55 volts[**].

The spectrophotometric analysis of Seeliger and Lindow has shown that the ozone bands fall off very abruptly in intensity in passing from the negative glow to the cathode dark space, the arc lines (O I) somewhat less abruptly, and the spark lines (O II) in general rather gradually. A visual study of the spectrum of the negative glow by the subjective method of Seeliger and Lindow showed that the green negative band behaved very much like the arc lines. No photometric study has been made for the ultraviolet and infra-red, but there is not any reason to suppose that the behaviour of lines and bands in these regions should be any different from that of the corresponding visible spectra.

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[*] Carmichael, see p. 362.

[†] Wrede, *Zeits. f. Phys.* liv. p. 53 (1929).

[‡] Geiger-Scheele, *Handbuch d. Phys.* xxiii. p. 760.

[§] Hogness and Lunn, Phys. Rev. xxvii. p. 732 (1926). The numbers have been slightly modified from those given by these authors.

[‖] Lockrow and Duffendack, Phys. Rev. xxv. p. 110 (1925).

[¶] Hopfield, Astrophys. Journ. lix. p. 114 (1924).

[**] According to previously mentioned spectroscopic data for O II and O III.

The Langmuir analysis * has shown that the ionization falls off very steeply from the negative glow to the cathode dark space, and more gradually towards the Faraday dark space, the negative glow being closely equipotential. Three groups of electrons are present, each with an approximately Maxwellian distribution of velocities, typical data concerning the brightest part of the negative glow in a 450 volt discharge in a tube essentially similar to that of § 2, with a gas pressure of 0·6 mm. Hg., being

Fast group	$3\cdot10^6$	per cc.	Average energy 17	electron-volts.
Secondary group	$3\cdot10^7$	,,	2·6	,,
Ultimate group	$1\cdot2\cdot10^9$	,,	0·3	,,

We will first calculate the number present in each group energetically able to effect ionization of the molecule at 15 volts in a single stage. This gives :—

Fast group $3\cdot10^6\epsilon^{-15/17}$ or $1\cdot3\ 10^6$ per cc.
Secondary group $3\cdot10^7\epsilon^{-15/2\cdot6}$ or $1\cdot0\ 10^5$,,
Ultimate group $1\cdot2.10^9\epsilon^{-15/0\cdot3}$ or $\bar{2}\cdot3\ 10^{-13}$ per cc.

The contributions of the two slow groups can be neglected, and the same is true to an even greater extent of their action in producing combined ionization and dissociation at 21 volts. The ratio of the number of electrons able to effect the 21 volt process to the number able to effect the 15 volt process is $\varepsilon^{-21\ 17}$; $\varepsilon^{\ 15\ 17}$, or 0·9. The positive ray analysis of Hogness and Lunn †, in which conditions may have approximated very closely to those in the negative glow ‡, would suggest a ratio of the concentrations of O_2^+ ; O^+ of about 7·1. The above inferences from the results of the Langmuir analysis are consistent with this, and with Seeliger and Lindow's and our observation that the bands and spark lines (O II) are of comparable intensity. It is shown later that no essential modification of this conclusion is required when dissociation is taken into account.

The feeble intensity of the O III lines and the absence

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* Carmichael, *loc. cit.*

† Hogness and Lunn, *loc. cit.*

‡ Morse and Gurney, Phys. Rev. xxxiii. p. 789 (1929).

of those of O IV is again consistent with the data for the electrons present.

No comment can be made upon the relatively feeble intensity of the ozone bands on our plates in absence of precise information as to how ozone is formed in the discharge.

A less satisfactory explanation can be given of the spectrophotometric results of Seeliger and Lindow, since only the critical potentials and not the excitation and ionization functions are known for oxygen. If these were known, however, they would have to be used in conjunction with the results of the Langmuir analysis for electrons moving in random directions, and not for any directed group of electrons supposed to be penetrating through the negative glow from the cathode dark space, since the work of Emeléus and Brown * has shown that the latter are practically absent under these conditions, except very close to the cathode dark space. Lack of knowledge of the excitation and ionization functions has also made it necessary to work in preceding paragraphs simply with the number of electrons energetically able to effect a process, irrespective of its probability. This is the best that can be done at present, but is unlikely to lead to serious error in the cases under consideration. In connexion with the results of Seeliger and Lindow, we may note however, that the form of the intensity-distance curves for the spectra is generally similar to that of the ionization-distance curves in such work as that of Emeléus and Brown. The maximum in the concentration-distance curve is also perhaps less sharp for the fast electrons than for the slow, as would be expected from the weak maximum in the intensity-distance curve for the spark lines (O II).

Another interesting point is that with certain exceptions the relative intensities of the spark lines (O II) in our tube correspond quite closely with their relative intensities in the positive column of a condensed discharge †. No analysis of the positive column has been made under these conditions with exploring electrodes, but we can predict with fair certainty that there must be present in the latter the fast group of electrons found in the negative glow of the more gentle discharge, with about the same energy, since otherwise production of the various excited states

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* Emeléus & Brown, Phil. Mag. vii. p. 17 (1929).

† Mihul, *loc. cit.*

of the O^+ ion could hardly occur at the same rates in the two cases. We can offer no satisfactory explanation of the absence of certain important O II lines (§ 2). There is, as already stated, little room for doubt that they have been correctly assigned, and it does not seem worth while to carry out the rather elaborate investigation which would be required to find which of the discharge factors was responsible for their absence from our tube. Seeliger and Lindow mention that the behaviour of the O II lines is somewhat erratic, indicating that their excitation functions are not all similar.

The nickel lines are probably excited largely by the electrons of the secondary and fast groups. Their sharpness speaks against their being excited by collisions of the second kind, and is also in accord with the absence of a large field in the negative glow *.

Oxygen is not well suited for observation of the continuous and diffuse spectra which are characteristic of the recombination of ions and electrons.

We have neglected the possibility that cumulative processes might be responsible for the ionization and dissociation. Any theoretical discussion of this must be very uncertain, but we can proceed approximately in the following way.

Under the conditions mentioned at the beginning of this section there are some 10^{16} molecules per c.c. The number of collisions in which direct ionization at 15 volts and at 21 volts can occur will be the product of the molecular concentration by the number of electrons energetically able to effect the process in question, viz. :

$$10^{16}\,3\cdot10^{6}\,\varepsilon^{-15/17} \text{ or } 1\cdot3\;10^{22}, \text{ at 15 volts} \quad . \quad . \quad . \quad (\alpha)$$

and $$10^{16}\,3\cdot10^{6}\,\varepsilon^{-21/17} \text{ or } 0\cdot9\;10^{22}, \text{ at 21 volts} \quad . \quad . \quad . \quad (\beta)$$

again multiplied by factors depending on (*a*) the average energy of the electrons (17 volts in this case) and (*b*) the probability of ionization for different speeds of the electrons.

If there are x times as many excited molecules present as ions, or approximately $10^{9}x$ per c.c., each with an average energy of excitation of 10 volts, the number of collisions in which these can be ionized will be the product of another probability factor by

$$10^{9}x\;\left(3\cdot10^{6}\varepsilon^{-(15-10)/17}+3\cdot10^{7}\varepsilon^{-(15-10)/2\cdot6}\right) \quad \text{or} \quad 10^{16}\,x. \quad (\gamma)$$

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* Frerichs, *Ann. d. Phys.* lxxxv. p. 362 (1928).

The ratio of this number to the number of direct ionizations at 15 volts is $5x10^{-7}$. The expression from which (γ) is derived contains two terms, each of which is arrived at in the same way as the single term above for direct ionization. The first represents the effect of the fast group, and the second that of the secondary group, which has now to be taken into account, although the slow group can still be ignored. 10 volts has been chosen as being between the 8 volt and 15 volt critical potentials for O_2, with a bias towards the lower of these. In view of the fact that the lower probably corresponds to dissociation, 10 volts is probably a considerable overestimate of the energy of excitation, which will make the subsequent calculations still more in favour of direct ionization at 15 volts.

Some measurements of anomalous dispersion made by Ladenburg * indicate that in the inert gases, under conditions similar to those in the negative glow, x is of the order 10^3. x would tend to be higher in the inert gases than in oxygen, since atoms can accumulate in metastable states in the former, but on the other hand the energies of excitation and ionization are more nearly equal in the inert gases than in oxygen. In the latter 10^4 seems a reasonable number to adopt, in which case the ratio becomes $5\,10^{-3}$. Even if the large target areas of excited molecules are taken into account, it is questionable if the differences in the probability factors could change this ratio to one of the order of unity or greater. K. T. Compton † has already suggested that it is ionization by single impact rather than by cumulative action which is of primary importance in Geissler tubes.

Returning to the effects of dissociation, we will consider a case when there are 10^{15} unexcited atoms per unit volume. The number of collisions in which they can be excited at 9·1 volts will be the product of a probability factor by

$$10^{15}(3\cdot10^6\varepsilon^{-9\cdot1/17}+3\cdot10^7\varepsilon^{-9\cdot1/2\cdot6}) \quad \text{or} \quad 3\cdot10^{21}. \quad . \quad (\delta)$$

and the number of direct ionizing collisions at 13·6 volts

$$10^{15}(3\cdot10^6\varepsilon^{-13\cdot6/17}), \quad \text{or} \quad 10^{21} \ . \ \ . \ . \ \ . \quad (\eta)$$

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* Ladenburg, *Zeits. f. Phys.* xlviii. p. 15 (1928), etc.

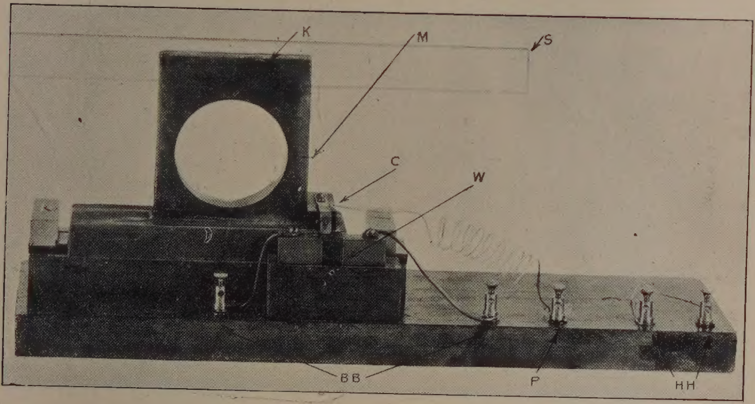
† K. T. Compton, Phil. Mag. xliii. p. 534 (1922).

It is also readily seen from a calculation similar to that performed on p. 390, that cumulative ionization may now lead to the production of ions at a rate comparable with (η). Comparing (η) and (β), we see that they are of the same order, but there is no reason to suppose that ionization of the atom directly will disturb to any large extent the otherwise existing balance between O_2^+ and O^+.

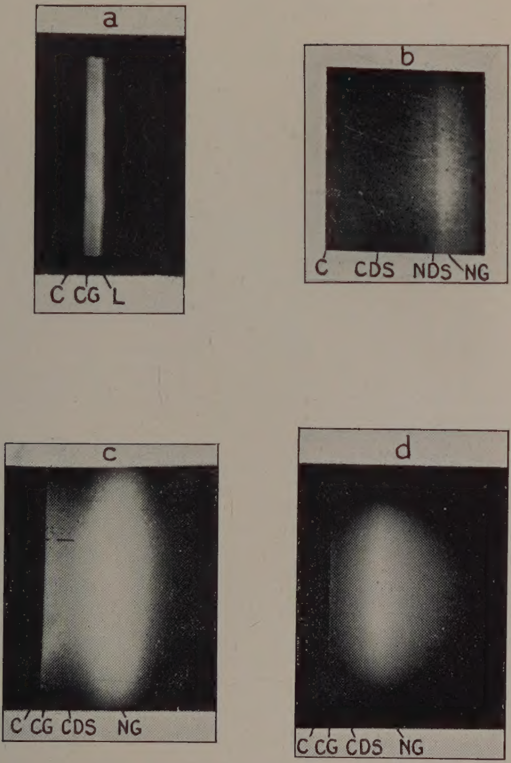
The remaining part of the spectrum to be considered is that of the neutral atom (O I). In the case of oxygen, we can see in a general way that these lines will not be enormously strong relative to the spark lines, since atoms, before they can be excited, have to be produced by processes energetically comparable with those producing ions from the molecules. In the inert gases, however, the arc lines are found to be less prominent than the spark lines in many instances, and it thus appears that there is some other factor which we have not taken into account which tends to promote radiation from ions. One obvious agency would be interatomic fields, but we are not able to say anything definite on this point.

The great difficulty in making calculations of the type attempted in this paper, apart from very incomplete knowledge of the probability factors, is that although the negative glow is not a system in thermodynamical equilibrum, yet interchanges of energy occur within it too frequently to be treated other than statistically. However, as is shewn by the occurrence of several groups of electrons, each with an equivalent temperature, it is, so to speak, half-way towards thermal equilibrium, and we can thus hope to obtain some idea of what is taking place by the methods which we have adopted. Perhaps the most striking fact emerging is the important part played by the fast group of electrons, the main function of the other groups, particularly the ultimate group, being, as elsewhere in the discharge, to effect the transport of the current in the tube. There is some similarity between the properties of the equipotential negative glow and the properties of ionized stellar atmospheres; the one is receiving energy unilaterally from the cathode dark space, and the other from the interior of the star, and this analogy may prove fruitful in future developments of the theory of the negative glow.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]



Instrument for measuring Magnetic Field Strength.



Cathode, C. Cathode glow, CG. Cathode dark space, CDS.
Negative glow, NG. New dark space, NDS.

a. Discharge through nitrogen. Cathode fall in potenial 380 volts. Pressure 0·82 mm. Hg. Current density 0·07 mA/cm.^{2} Ilford special rapid panchromatic plate. Magnification 1·81.

b. Oxygen, 450 volts, 0·25 mm. Hg, 0·04 mA/cm.^{2} Ilford special rapid panchromatic plate. Magnification 1·18.

c. Nitrogen, 400 volts, 0·53 mm. Hg, 0·05 mA/cm.^{2} Ilford special rapid panchromatic plate. Magnification 1·37.

d. Oxygen, 420 volts, 0·33 mm. Hg, 0·09 mA/cm.^{2} Imperial panchromatic plate. Magnification 1·04.